











**HANDBOOK OF  
CHEMICAL MICROSCOPY**

VOLUME I

Principles and Use of Microscopes and Accessories  
Physical Methods for the Study of Chemical Problems

# HANDBOOK OF CHEMICAL MICROSCOPY

BY

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VOLUME II

Chemical Methods and Inorganic Qualitative Analysis

*SECOND EDITION*

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## PREFACE TO THE SECOND EDITION

In the preparation of this revision of Volume II of the *Handbook of Chemical Microscopy* the authors have felt justified in retaining in their original wording such portions of the first edition as have stood the test of usage, except where there appeared to be obscure or incomplete descriptions or directions.

Comparatively little entirely new apparatus and procedure has met the requirements of practical applicability in the laboratory.

The authors have drawn freely from the more recently published literature of chemistry and have tried to give due credit therefor. They are indebted to the invaluable critical studies of Doctor M. N. Short and Doctor L. C. Staples, and are grateful to Doctor T. G. Rochow for many suggestions.

E. M. C.  
C. W. M.

CORNELL UNIVERSITY,  
*September, 1939*





## PREFACE TO THE FIRST EDITION

In spite of the continual growth which microscopical qualitative analysis has undergone, it is noteworthy that the methods of this branch of chemistry, as taught by Behrens in the early nineties, stand with little need for modification. Additional tests have been devised, new reactions and manipulative procedures have been utilized, but few of those which he first proposed have failed to stand the test of the last forty years. Building better than he knew, he chose reagents which are still unexcelled for convenience, rapidity, and versatility.

The development of microscopical qualitative analysis has been largely in the direction of new specific tests and identity reactions for relatively pure materials, rather than of new group reagents. Modifications of technique and of apparatus have been numerous, and the applications of microscopical tests have extended to the most diverse fields of chemistry and its related sciences.

Some of these applications are of long standing, though the methods have been improved and amplified in the course of years. The identification of mineral grains in ores and rocks; of the inorganic constituents in plant tissues, foods, and vegetable drugs; and of the various raw materials and products of chemical and other industries, are fields in which the uses of microscopical qualitative analysis have shown particular expansion, and in which many new procedures have originated. Although the present volume is limited to inorganic analysis, the manipulative technique and general principles will be found applicable to studies of organic reactions.

Any work on analytical chemistry, unless it ignores all previously existing and tested procedures, must be in large part a compilation; the present one is no exception. The authors acknowledge first of all their indebtedness to Behrens' fundamental contributions. They have made little attempt to cite in detail the original sources of reactions and tests which have long been the common property of chemists, and they make no claim to originality except in regard to a small proportion of the methods presented.

However, the choice of reagents and technique has not been without discrimination, and only methods which hold promise of general usefulness in microscopical analytical work have been included. All but the newest ones of these have been tested not only by the authors but also in the hands of students, and the various precautions indicated, though

perhaps unnecessarily detailed, have been based on the difficulties likely to be encountered by workers having only an ordinary knowledge of inorganic and analytical chemistry.

The inclusive field of "microchemistry," which comprises all chemical procedures dealing with small amounts of material, is discussed only as regards those portions of it which involve microscopical qualitative reactions. Quantitative methods, volumetric and gravimetric, are therefore omitted; quantitative microscopical analyses of heterogeneous mixtures are discussed in Volume I.

Brief experiments are given to illustrate the behavior of the more common elements, and to constitute the basis for a course of instruction in microscopical qualitative analysis.

In response to repeated requests, photomicrographs of most of the common and useful tests have been included, not without some misgivings, for the authors believe that the mere examination of pictures will not take the place of the preparation and direct study of actual tests. The user of this book is urged to carry out the various experiments, and others which will suggest themselves, and to see for himself not only the commonly prevailing types of crystals which have been selected for the illustrations, but also the variations from these "normal" appearances. Only by so doing can he acquire the experience and judgment in interpretation, and the manipulative skill, which are essential to intelligent and rapid analyses. If he will accompany this study by reference to the standard works on inorganic and analytical chemistry, he will find the procedures instructive in their chemical significance as well as a profitable means of rapid and direct analysis.

Volume II, like Volume I, is based upon *Elementary Chemical Microscopy*; the pages therein devoted to qualitative analysis have been entirely rewritten, greatly expanded, and presented from a somewhat different angle.

In the preparation of the book which is now superseded by this Handbook the senior author was greatly indebted to his friends and teachers, Professor S. H. Gage of Cornell University, Professor Th. H. Behrens of the Polytechnic School of Delft, and Doctor E. Macé of the University of Nancy — pioneers in the science and art of applied microscopy — and he would be ungrateful, indeed, did he not acknowledge how much of their precepts, opinions and methods are reflected in the present volume.

E. M. C.  
C. W. M.

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# HANDBOOK OF CHEMICAL MICROSCOPY

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## INTRODUCTION

In Volume I of this Handbook the observations of physical and physicochemical phenomena have been discussed in their relation to qualitative analysis, to the study of industrial materials, and to the solution of problems arising in research. It is there shown that such observations often may be sufficient to establish the identity or the composition of a substance in question without the necessity of having recourse to chemical reactions.

Frequently, however, qualitative chemical analyses are required. These, when made by microscopical methods, enable the analyst to obtain results in a minimum of time, upon a minimum of material, with the expenditure of little labor and at a wholly negligible cost, and all with no sacrifice of accuracy.

Because only small amounts of materials are employed, speed is assured. Obviously a fraction of a cubic centimeter can be evaporated, decanted, or filtered in less time than will be required to perform the same manipulations with 100 cc. or 10 cc. If the methods are speedy, results are to be obtained with corresponding rapidity.

But speed and ability to analyze very minute amounts of material are not the only advantages of "microanalysis"; many of the "micro" tests for cations and for anions are far superior in their certainty and dependability to the macroscopic tests for the same elements or compounds.

Microscopical qualitative chemical analysis requires a special technique, which, however, is readily acquired.

It is the aim of Volume II of this Handbook to describe the essential manipulative methods in detail and to present a compilation of the most dependable tests for the inorganic cations and anions.

In the selection of the tests discussed, the authors have been guided more by the applicability of the tests to the analysis of complex mixtures and by the certainty of the results obtained than by sensitivity of reaction. Many of the statements regarding sensitivities, interferences,

or applicability of tests will be found at variance with the published results of others, usually in the direction of less optimistic conclusions.

Numerous interesting "micro" reactions are omitted, either because they are suitable only as identity tests on substantially pure substances and are of little use in mixtures of various unknown materials, or because they require a more precise control of concentrations, acidity, temperature, etc., than is practicable in a single drop of unknown composition on a microscope slide.

Those reactions of doubtful value which are discussed have been found useful in special cases or have been deemed of sufficient pedagogical interest in the consideration of group relations to warrant their being called to the attention of the analyst. Otherwise, with few exceptions, reactions have been included only if they will yield results under almost any conditions and in almost any combinations.

Color reactions and spot tests<sup>1</sup> are not discussed except in a few instances, because they do not involve microscopical observations or technique.

The incompleteness of the present work may perhaps be excused on two counts:

A large proportion of published methods and tests (both "micro" and "macro") are not described with reference to their behavior when applied to mixtures, and it has not been possible as yet to study all the interferences which undoubtedly exist.

In this class are to be found those reaction products formed by the direct addition of a metallic salt to an organic compound. Most of the recently proposed "micro" qualitative tests are of this nature and are of limited application in the analysis of material of unknown composition because both the cations and the anions of the salts are involved in the formations of the crystals which may separate in the test drops, crystals whose habits are influenced as much by anions as by cations; hence the number of combinations possible may be very great. Few tests involving these interesting compounds have been included in this edition of the Handbook.

<sup>1</sup> See especially the work of Feigl and his pupils:

Feigl and Stern: *Zeits. anal. Chem.* 60, 1 (1921).

Feigl and Neuber: *ibid.* 62, 369 (1923).

Feigl: *Mikrochemie* 1, 4 (1923); 6, 50 (1928).

Feigl: *Tüpfelanalyse*: pp. 137-146 in Emich's *Mikrochem. Praktikum* (1931).

Feigl-Mathews: *Qualitative Analysis by Spot Tests* (1937).

Heller: *Mikrochemie* 1, 213 (1929); 8, 33 (1930).

Holzer: *ibid.* 8, 217 (1930).

Engelder, Dunkelberger, and Schiller: *Semi-Micro Qualitative Analysis* (Wiley, New York, 1936).



A limited number of reactions are available for certain metals and acids, and although there is great need of discovering new ones or adapting existing reactions to microscopical use, a vast amount of investigation remains to be done. Until these necessary investigations have been carried further, serious gaps will exist in microscopical analytical methods. These shortcomings, however, are hardly more serious than those of macroscopic qualitative analysis, in which the various systems work nicely on a selected list of the more common ions but are spoiled by intruders.

In selecting methods for microscopical analysis, ease of manipulation has been an important consideration, even at the expense of sensitivity or minuteness of sample. Tests requiring special apparatus or successive separations have largely been omitted, as contrary to the chief advantages of chemical microscopy: ease and directness.

As teachers of the science of chemistry the authors have felt called upon to lay stress upon the chemical properties of the different ions discussed, particularly in their relations to each other and in their behaviors in microscopical qualitative analysis. For pedagogical reasons a very brief outline of properties has been presented as an introduction to each "group" or "family" of elements or ions. These discussions are intended as mere summaries and rough generalizations, and like most generalizations are not always strictly accurate.

Such comparative studies are, however, particularly useful in connection with families of the elements according to the Periodic Classification, and exemplify some of the most beautiful relationships in the whole field of chemistry. The crystallographic similarity and interchangeability of chemically similar elements in compounds, embodied in the principle of "isomorphism," has been stressed whenever it has a bearing upon the reactions discussed, for it must constantly be borne in mind in microscopical analysis, and its importance is not sufficiently emphasized in our teaching of general chemistry.

## CHAPTER I

### MANIPULATIVE METHODS OF A GENERAL CHARACTER. HANDLING SMALL AMOUNTS OF MATERIALS

The manipulative methods or processes most frequently necessitated in qualitative analysis are:

1. Testing for solubility.
2. Bringing the material into solution; sometimes called "opening up the material."
3. Decantation.
4. Filtration or centrifugal separation.
5. Sublimation.
6. Distillation.
7. Fusions and ignitions.
8. Applying reagents.

**Testing for Solubility and Heating Test Drops.**—This is the preliminary step in all chemical analyses and should always be carried out in a thoroughly systematic manner.

At the corner of a scrupulously clean object slide<sup>1</sup> place a small drop of water (or other solvent). Spread it out with a glass rod or platinum wire so that it occupies a circular area about 4 or 5 mm. in diameter and is about  $\frac{1}{2}$  mm. deep. Closely adjacent to this drop (about 2 mm.) place a tiny fragment of the material to be tested.

Transfer the preparation to the stage of the microscope and focus upon the edge of the drop nearest the fragment to be tested. Use a low power and see that the illumination has been properly adjusted.

By means of a rod or wire or a stiff hair, slowly push the fragment into the drop of solvent, and study the preparation at once. Note well the phenomena which may take place. The substance may merely melt away; it may hydrate or form another salt; it may dissolve with decomposition and a precipitate may be formed; it may give off bubbles of gas; or it may remain unchanged.

If, after a few seconds, there appears to be no change in the size or in the appearance of the fragment of the material being tested, warm the drop gently by holding it a second or two about one centimeter

<sup>1</sup> See *Vol. I*, page 172.

above a "micro" flame. (*F*, Fig. 1. See also page 137, *Vol. I.*) The tiny flame should be so regulated as to be not over 5 mm. high. Cool the preparation quickly by bringing it in contact with a cool metal surface (base of the microscope or a metal block or plate). Examine the preparation and note whether there is now any change in the fragment indicating solubility in warm water.

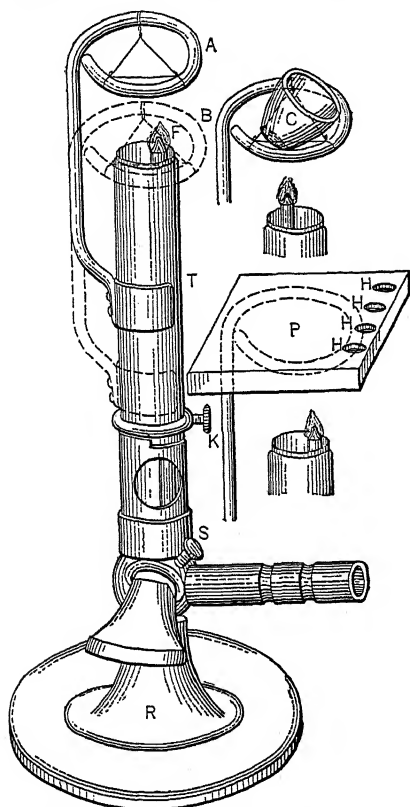


FIG. 1. Micro Burner with Support Ring and Hot Plate.

Testing for solubility in boiling water requires a somewhat larger test drop or a crucible. Tip the slide at an angle as shown in Fig. 2. Lower it so that the slide just barely touches the tip of the micro flame and see that the heating is done just under the upper edge of the drop. Move the slide slowly back and forth above the flame but avoid tipping from side to side. These precautions are usually necessary in

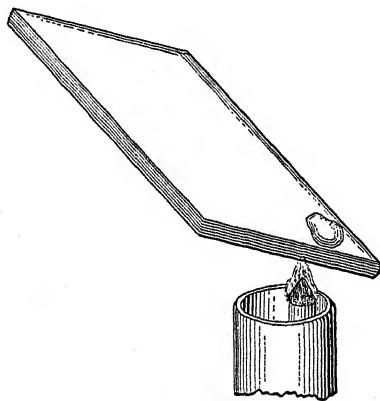


FIG. 2.

order to prevent the drop from creeping up and spreading over the surface of the object slide, especially when the solvent is not water.

Watch closely and as soon as bubbles are formed remove from the flame and *cool instantly* by bringing the slide in contact with a cool metal surface. Unless this is done, all the liquid will evaporate. It is essential to work quickly.

If the analyst is not restricted to very minute amounts of material, tests for solubility can be performed more conveniently in small crucibles and a drop of the solvent placed upon an object slide and evapo-

rated for examination. When dealing with organic solvents having high volatility or low surface tension, the crucible method is preferable to that of operating upon the object slide. In all cases a "blank" should be made under conditions similar to the experiments performed upon the material in question, in order to eliminate the effect of possible impurities in the solvent.

Never place a hot slide upon the stage of the microscope, for the surface of the stage may be seriously damaged; moreover, vapors may arise from even moderately warm preparations and may condense upon the objective, injuring it.

If the tip of the micro flame is brought into contact with the object slide, more or less lamp black is almost always deposited upon the under surface of the slide. This film must be wiped off with lens paper or a cloth before the preparation is examined. If this is not done, fine details may be obscured or the color of reaction products may be misinterpreted.

Since the test drop was placed at the corner of the slide, there is no danger of breakage on heating.

To determine whether any material has passed into solution, decant the liquid from the undissolved material (see Decantation, page 10), and evaporate to dryness by gentle warming, being careful to avoid heating the preparation after it has gone to dryness.

It is impossible to obtain object slides made of glass sufficiently resistant that boiling water and acids will exert no marked solvent action upon them. Even the so-called "non-corrosive" object slides now on the market yield residues which are readily appreciable under the microscope; but these slides are much superior to those of more easily attacked glass. Alkaline solutions will, of course, attack them in the cold. The results of tests for solubility should always be checked by comparison with the residues left when the solvent alone is evaporated under exactly the same conditions.

In highly critical investigations where the presence of mere traces of glass components other than silica will be objectionable, object slides of fused silica can be employed. If silica must also be absent, celluloid slips or glass object slides coated with "Duco," "Bakelite," or other base varnish must be used.

Tests for the solubility of substances in boiling corrosive liquids such as strong acids, alkalis, etc., should be performed on clean, bright platinum foil; the solvent should then be decanted, concentrated, and only transferred to a glass or silica or celluloid slide when evaporated almost to dryness.

Since illuminating gas usually contains appreciable amounts of vari-

ous compounds of sulphur and ammonia, an alcohol lamp should be employed as the source of heat when "traces" of either sulphur or ammoniacal nitrogen are to be sought in material of unknown composition.

If the substance whose solubility is being tested is subsequently to be analyzed, a sufficient quantity of it is tested on glass, quartz, or platinum, according to the necessities of the case, care being taken to observe the precautions given above, and to make a "blank" upon the water and reagent alone. A residue obtained by evaporation may not always be due to the action of the solvents on the glass but may result from impurities in the solvent.

When more than one solvent has been found, the proper selection will be governed by many circumstances. It is obvious that no rule may be given which will apply to even a majority of cases. Much must always be left to the judgment of the analyst.

**Evaporating to dryness upon an object slide** should be performed at a gentle heat only. Warm the preparation, holding it one or two centimeters above the flame, then remove it from the flame and blow gently upon the warm drop; heat again, and again blow; repeat the process until the solvent has been driven off. If this method is followed, a uniform, closely adhering film will result instead of irregularly distributed loose particles, and the danger of loss through decrepitation of the tiny solid particles is avoided.

In the absence of gas an alcohol lamp provided with a wick-tube so small as to yield a flame not over 5 mm. high will be found to answer all purposes where a "micro" flame is essential. In testing for the presence of sulphur in compounds or in heating material where sulphur may enter into combinations prejudicial to reactions or tests, an alcohol flame is necessary since nearly all fuel gases contain sulphur compounds.

When the work table can be serviced with electric current, heating devices of varied types and forms can be easily and quickly made from resistance wire ("Nichrome," "Advance," etc.)<sup>2</sup> placed in series with a lamp bank or rheostat. Heating units of this kind will be found to be satisfactory and convenient.

Electric cigar lighters<sup>3</sup> are being used in several laboratories, either directly or built-in as illustrated in Fig. 3, page 8. These electric microstoves are made from a ten-cent cigar lighter screwed into a standard-size socket in series with a rheostat (100 ohms, 1 amp.) and a small tumbler switch.<sup>4</sup>

<sup>2</sup> For characteristics see Lange's *Handbook of Chemistry* (Handbook Publishers, Inc., Sandusky, Ohio, 1937), pp. 652, 653.

<sup>3</sup> Obtainable from the Rodale Mfg. Co., Emaus, Pa.

<sup>4</sup> T. G. Rochow, personal communication.

Electric heating devices possess a number of advantages over gas; there are no deposits formed upon the under side of the heated object slide, nor are oxidation products of gas present which are absorbable by the test drops upon the object slide and which may seriously interfere with certain sensitive tests. The heat is more easily controlled and duplicated.

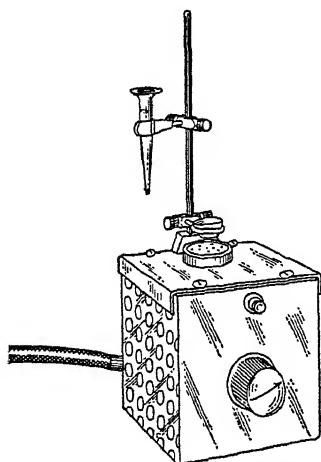


Fig. 3. Royer-Rochow "Micro" Electric Stove.

**Evaporating in a Current of Hot or Warm Air.**—If compressed air (blast) is available at the work table, evaporation in a current of heated air is convenient and time saving, particularly when dealing with inflammable solvents or materials requiring care lest they be heated to too high a temperature or in the evaporations of solvents which exhibit a marked tendency to "creep" when warmed in watch glasses or in micro crucibles. In such cases gently blowing warm air over the surfaces of the preparations is preferable to heating over a micro flame. A device for this purpose is shown in Fig. 4. It consists of a quartz Y-tube provided with an internal coil of fine platinum wire (about 0.13 mm.

wire) heated by an electric current regulated by a suitable resistance. The coil is doubled upon itself with a mica septum between the halves. This septum should be at right angles to the position in which it is shown in the diagram so that there may be a free flow of air over each half of the coil. The entering air should of course be filtered.

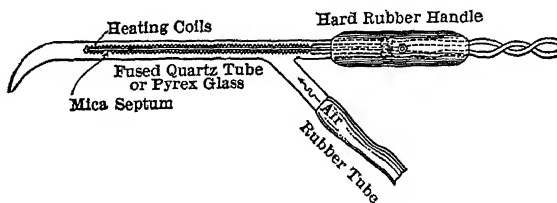


Fig. 4. Apparatus for Evaporating in a Current of Hot Air.  $\times \frac{1}{2}$ .

**Bringing the Material into Solution.**—When the solubility test shows that the material is practically insoluble in water, trials must be made to ascertain a suitable solvent. The fragment is tested with various possible solvents both cold and hot.  $\text{HNO}_3$  and  $\text{HC}_2\text{H}_3\text{O}_2$  are the most satisfactory from the point of view of qualitative analysis.

If silicates or analogous compounds are suspected and must be brought into solution for testing for cations, it is just as well to pass at once to  $\text{HF}$ , or to crystals of  $\text{NH}_4\text{HF}_2$  and an acid. In such an event, solution must be brought about on foil or in a cup of platinum, or upon a celluloid

or cellulose acetate object slide, and care must be taken to observe all the precautions mentioned under Method X, page 43.

When alcohol or similar liquids of very low surface tension are used, it is more convenient to treat the material in a container such as a small crucible (Fig. 10, page 17) or a hollow slide, and thus avoid the "creeping" of the solvent over the object slide. Holding the slide almost vertical reduces the creeping to a minimum, and if held in this position for a few seconds most of the volatile solvent will have evaporated and the drop of liquid remaining can be transferred to another inclined slide with little difficulty. The decanted drop usually creeps but little.

To ascertain whether alcohol or other analogous solvents have material in solution, it is often necessary to confine the evaporation to a small circular area in order that the residue may be studied. A satisfactory procedure is to take up the solvent in tiny tubes drawn down to hair dimensions. Touching these tubes to the liquid partly fills them by capillarity. A tiny drop is expelled upon a clean slide. Evaporation is so rapid, especially if the slide is slightly warm, that the drop cannot spread. When dry, another drop is forced out of the capillary tube and applied to the same spot as the first. The operation is continued until it becomes apparent whether any solvent action has taken place; the amount and character of the residue give the required information.

Many inorganic materials require treatment with concentrated acids or ammonium hydroxide or the fixed alkalis to bring them into solution. Preparations consisting of drops of strong HCl, HNO<sub>3</sub> aqua regia, or NH<sub>4</sub>OH should be placed upon the stage of the microscope for as short a period as possible so as to reduce danger of injury to the objectives. Preparations of this sort should be covered with a cover-glass, or the objective should be protected by a cover-glass held in place by a drop of immersion oil; or the device shown in Fig. 28, page 43, may be used.

When metals or alloys are to be brought into solution, care should be taken to dissolve them completely, and to test any non-metallic residue remaining. It is often sufficient to collect the sample by means of a ground glass slide, on which a "streak" is rubbed off. A drop of acid serves to dissolve the metal; the solution may then be decanted and tested further. By using a hollow slide, the concavity of which is roughly ground, more acid can be used and the solution can be carried out on a somewhat large scale.<sup>5</sup> For filings or fragments of metals, a micro crucible will be found indispensable. Extraction of soluble constituents may be necessary, either for their analysis, or to facilitate

<sup>5</sup> Strebinger and Holzer: *Mikrochemie* 8, 264 (1930).

examination of the insoluble residues.<sup>6</sup> This may be carried out in small tubes, with centrifuging, or by means of microextraction apparatus at elevated temperatures.

**Decantation.**—The separation of a clear liquid from most precipitates or undissolved residues in as small volumes as single drops can ordinarily be accomplished without difficulty by decantation. Precipitates which float can be subjected to the treatment described below.

Success is largely dependent upon the use of object slides so scrupulously clean that a drop of water can be made to "wet" the surface of the glass and can be made to flow in a narrow continuous channel without breaking into a number of droplets. Object slides that do not permit the spreading out of a drop of water when stirred should be discarded, for the liquid cannot be satisfactorily drawn off if the surface of the slide is not free from an objectionable film.<sup>7</sup>

Hold the slide in a horizontal position. Carefully introduce the end of a drawn-out glass rod into the drop near the circumference. Draw the rod slowly and lightly across the slide, and at the same time slightly incline the slide in the direction of the path of the rod. Liquid will follow the rod in a narrow channel and, providing the movement is very slow, there will be little or no disturbance of the precipitated material. Having moved the rod for several millimeters from the test drop, it is given a very slow circular motion, thus spreading the channel into a drop. This spreading out of the liquid upon the slide induces a flow from the test drop into the newly formed drop. The flow is facilitated by inclining the slide more and more and, when the new drop is sufficiently large, or, when practically all the supernatant liquid has been drawn off from the test drop, the rod is withdrawn. The preparation should now consist of two drops connected by a narrow channel as shown in Fig 5. A piece of folded filter paper is rapidly drawn across the channel *C*, Fig. 5, thus separating the two drops, and the preparation heated gently at *C* over the micro flame, to dry the slide at this point and thus prevent a back-flow of the decanted liquid. The slide can now be placed in a horizontal position, and either the residue in the test drop or the liquid in the decanted drop subjected to such further treatments as may be necessary.

<sup>6</sup> Apparatus for the extraction of vehicles from paints, in the analysis of pigments, is described by Hetterich: *Mikrochemie* 10, 379 (1932) and Gettens: *Tech. Studies Fine Arts* 2, 107 (1933).

<sup>7</sup> For methods for cleaning object slides, see *Vol. I*, p. 172. To avoid the annoyance of object slides with repellent films upon their surfaces, they can be kept submerged (after treatment with "cleaning mixture" and washing) in 95 per cent ethanol, from which they are removed with forceps, flamed and cooled immediately before use.



The essential points to be observed are the proper angle of inclination of the slide, the rate and manner of spreading out the drop of the drawn-off liquid, and the cutting of the channel without absorption of too much liquid by the filter paper.

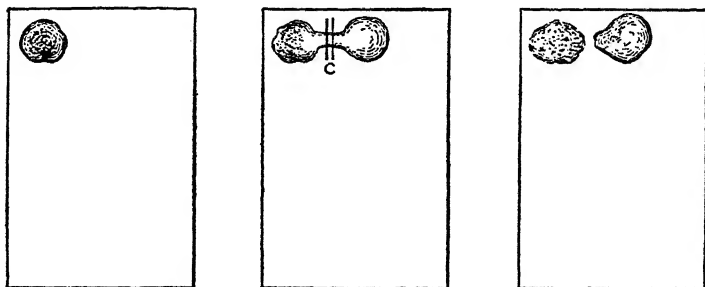


FIG. 5.

When an accumulation of solid matter forms a dam at the head of the channel and thus interferes with or prevents the flow of liquid, it is usually better to start a new channel to one side of the dam, for if breaking the dam is attempted the probability is that sediment will flow into the drawn-off liquid.

If the decanted liquid is not wanted for other tests, the decanted drop and connecting stream are wiped off the slide with filter paper, and the area they occupied warmed gently to dry it. It is frequently sufficient merely to introduce the edge of a thick piece of filter paper into the drop, removing the liquid by imbibition and simultaneously shoving the precipitate together into a small heap. This procedure is particularly convenient when decanting from a very small drop.

Not infrequently the suspended matter in the test drop persists in flowing over with the decanted liquid. When this occurs and heating the preparation is permissible, the following procedure may be adopted. Tip the slide so as to cause all liquid and suspended matter to flow back again into the test drop. Warm the preparation so as to dry the slide and prevent further flow of liquid. Evaporate the test drop to dryness by warming and blowing upon the preparation, carefully avoiding heating just as the drop becomes dry. Treated thus, the sediment generally adheres to the surface of the slide, and if a drop of water (or original solvent) is now carefully added the soluble materials will be dissolved, and the insoluble portion remains agglutinated and ordinarily adheres to the surface of the slide; decantation can then be practiced without much danger of a flow of sediment.

Even if the decanted liquid is not perfectly clear but contains a few

particles of the material under treatment or of the precipitate which has been formed by the addition of reagents, it will generally be found to be satisfactory for subsequent tests.

A precipitate is washed by adding to the test drop drops of water or other solvent and decanting after each addition and digestion.

When a number of drops are obtained in the process of washing, and all of them must be saved and united for subsequent examination, it is best to transfer them to a second clean slide; this is done by decanting into the extreme corner of the slide, cutting off the stream with filter paper, and warming as already described. Now slowly raise the slide to an almost vertical position and bring the corner, holding the decanted drop, in contact with the slide prepared to receive it. Touch the drop at the corner with a drawn-out glass rod or platinum wire and the drop will flow at once onto the slide below. Raise the vertically held slide and warm the wet corner over the micro flame. Wash the residue as before and again transfer. The united washings may afterward be concentrated to the proper volume by evaporation.

In all cases where decantation is to be practiced, the size of the drop to be treated should be somewhat larger than that employed in tests with reagents requiring no separation of liquid from solid.

**Decantation by Means of Capillary Tubes.** — The removal of part or all of the liquid of a test drop by means of slender capillary tubes may be classed as a method of decantation. Thin-walled glass tubing is drawn out into slender tubes having bores not greater than 0.75 mm. and very thin walls. Cut into lengths of about 6 cm., these tubes will be found of constant use, especially when the removed liquid is to be rejected. The conditions of the test drops and of the precipitate should be the same as described above for ordinary decantations. The capillary tube is carefully introduced into the drop in a vertical position and slowly inclined until almost horizontal so as to cause the liquid to rise in the tube and is then carefully withdrawn without stirring the drop. If the liquid in the tube is to be subjected to tests, the tube is set aside; but if of no further use the capillary and its contents should be thrown away.

For removing liquids from drops or applying drops of reagents to specimens or to object slides, F. C. Calkins<sup>8</sup> has suggested a form of tube which he has termed "the drinker." Its construction and use will be apparent from Fig. 6, page 13. The drawn-down end of the tube should be smoothed in a flame and ground smooth and true on a fine stone so that its plane forms an angle of 30° with the axis of the tube.

**Centrifugal Separation.** — Some type of centrifuge is an almost indispensable accessory for every laboratory concerned with problems involving small amounts of material in either synthetical or analytical

<sup>8</sup> The Transfer of Grains from one Liquid to another; *Amer. Mineralogist*, 19, 143 (1934).

procedures. No apparatus other than the microscope can be made such a time and labor saver. Centrifugal separations are far superior to any filtration system when dealing with small volumes of liquid having very small amounts of solids in suspension, since there is no loss of either

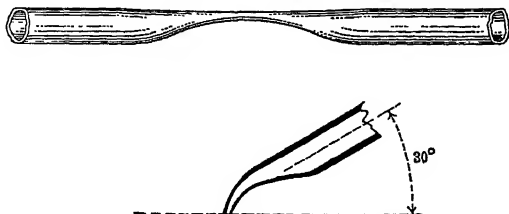


FIG. 6. Calkins Pipette for Transferring Drops.

precipitate or "centrifugate," neither is there any admixture of foreign material (fibers, etc.). When dealing with suspended matter of almost colloidal dimensions, filtration is usually impracticable (as, for example, solutions milky with finely divided sulphur).

Since the suspended matter is thrown out in the centrifuge tubes in a compact mass, the liquid above can be separated easily and the precipitate thoroughly washed with any liquid not attacking glass. After washing, the precipitate can be dried in the tube and treated if desired with a series of non-aqueous solvents, centrifuging in turn after each solvent.

Certain phases of centrifugal separation have been discussed in *Vol. I*, page 146, *q.v.*

Of the many models of centrifugal machines, electrically driven types with rheostat speed control will be found most convenient. Of the smaller machines those with "haematocrit" attachment are better fitted for handling very small volumes of liquid which contain very small amounts of fine, dispersed, suspended matter, not only because smaller tubes can be more conveniently handled but because the horizontal "haematocrit" attachment permits of much higher speeds than can be obtained with the small machines having only the hanging-tube heads.

Tubes for the treatment of volumes of liquid less than one cubic centimeter can be inexpensively and quickly made by drawing out glass tubes rather abruptly and heating the drawn-out and sealed end so as to thicken the end slightly. After centrifuging, the clear, supernatant liquid is removed by means of a capillary pipette and the tube cut off just above the precipitate, thus making it readily accessible.

**Filtration.** — The separation of a liquid from a precipitate is not always practicable by decantation. The precipitate may be so light or so finely dispersed or the surface tension may be such as to cause

the crystals to float upon the top of the test drop, making decantation impracticable. Under these circumstances, filtration is necessary.

The filtration of a drop upon an object slide is most satisfactorily accomplished by means of a filtration tube.<sup>9</sup>

A modification of the straight tube which we have found convenient is shown full size in Fig. 7. The lower end is ground smooth and true and exactly at right angles to the axis. To the upper end a

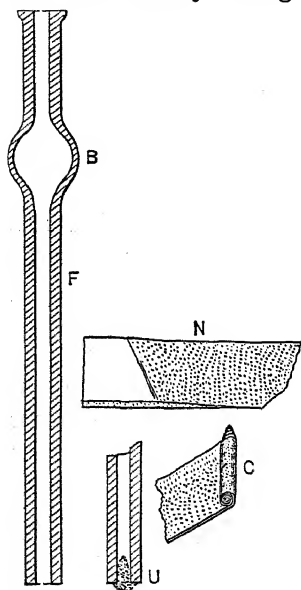


FIG. 7. Tube for Micro-filtration.

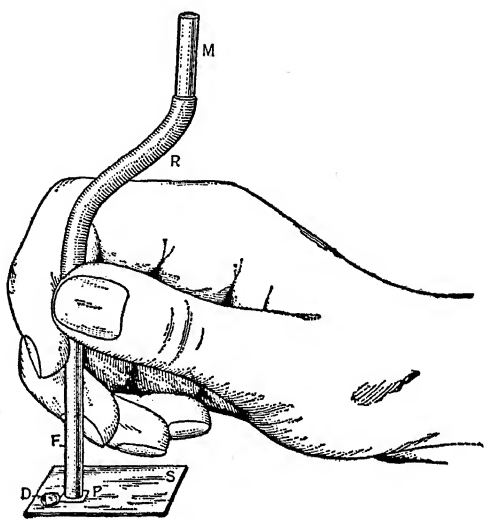


FIG. 8. The Behrens-Hemmes Method of Microfiltration.

piece of soft rubber tube about 80 mm. long is attached. See Fig. 8. The short piece of glass tube *M* serves as a mouthpiece. The filter tube is cleaned by pushing through it, by means of a stout brass wire, a plug of damp lens paper or filter paper.

The filtering tube may be used in either of two ways, depending on the quantity of liquid and its location. For a small drop on a slide, from which the precipitate must be recovered, the following method is preferable. A piece of filter paper, thick and soft but of a rather close texture, is selected; a piece cut from a small size "extraction thimble" or from a strip of the paper used for the determination of fat in milk will prove satisfactory. A small square is cut from this paper, of such a size as to be not quite 1 mm. larger than the diameter of the filter tube.

<sup>9</sup> There appears to be some doubt as to the originator of the principle involved. It was in use by Behrens in 1898 and was described by Hemmes in 1898, *Rec. Trav. Chim. Pays-Bas* (II) 16, 369.

The little square is conveniently cut upon a cork support with a very sharp knife, using a sawing motion so as to avoid unduly compressing the paper. It is then placed upon the object slide *S*, Fig. 8, which lies horizontally upon the table top, and the square is carefully moved until it occupies a position *P* closely adjacent to the drop to be filtered, *D*. The *ground end* of the filter tube is pressed lightly but firmly against the filter paper in such a position that the paper projects slightly beyond the tube. The whole is then moved slowly forward into the test drop. As soon as the paper has become wet through, gentle suction is applied to the upper end of the tube by the mouth, through the agency of the rubber tube. At the same time the filter paper is slowly advanced still further into the drop; the precipitate, unless exceedingly fine, will be pushed along in a ridge before the advancing paper and the liquid will rise in the tube. Care must now be taken to keep the rubber tube slightly curved, as shown in the cut. When sufficient liquid has risen into the glass tube, suction is discontinued; the rubber tube compressed at its upper end between the fingers and is simultaneously straightened to prevent the forcing out of the liquid. To lift the tube from the slide and the piece of filter paper, stretch the rubber tube very gently and raise the whole apparatus.

The filtrate contained in the tube is removed by bringing the ground end in contact with a slide and bending the rubber tube, the upper end of which is kept closed; the liquid will generally flow out at once; if not, straighten the tube, open the upper end, and blow *very gently*, but only just sufficiently to expel the drops.

A little practice is required to gauge the proper pressure of the tube upon the filter paper and to maintain this pressure uniformly without tipping the tube out of its vertical position, or pressing so hard as to make difficult the sliding forward of the tube and paper.

Too strong suction applied to the tube will cause the entrance of air, and there is then danger of sucking the liquid up into the mouth. This is particularly likely to happen if the test drop goes dry. The bulb *B* in the tube, Fig. 7, page 14, is designed to guard against this danger.

Unless the rubber tube is pinched and stretched just at the instant that the apparatus is lifted off the filter paper, the contents of the tube may flow back upon the slide.

Where larger amounts of liquid are available, or are contained in some vessel, and where a small loss of precipitate is of no importance, the filtering tube may be used in another manner. Savage<sup>10</sup> has sug-

<sup>10</sup> *Jour. App. Micros.* 3, 678 (1900). The principle involved is very old. Filtering tubes with paper or asbestos fibers in their bore were advocated many years ago to filter volumes of about 1 cc.

gested the insertion of the filter paper into the bore of the tube. The same filter tube, Fig. 7, may be used. A long narrow strip of filter paper *N* is cut on a bevel as shown in the illustration and is rolled between the fingers into a rather tight, slightly tapering cigar-shaped plug *C* just large enough in diameter to fit snugly in the bore of the tube. When the unrolled portion of the paper strip is removed it should be done with a slanting tear so as to leave no ridge along the filter plug.

The long plug is inserted tightly into the tube, tapering end up. It should not have over 4 to 6 mm. within the tube. The projecting part is cut off about 1 mm. from the end of the tube, using a sharp knife with a sawing cut against cork. The projecting end is then "upset" with the knife blade as shown in Fig. 7, *U*, page 14.

The plug is first moistened with the same sort of liquid as is to be filtered and is dipped directly into the test drop. Suction is applied by the mouth through the rubber tube. The clear liquid rises in the tube. When sufficient filtrate has been obtained, suction is discontinued and the tube lifted out of the test drop.

The filtrate can be removed by means of a capillary pipette, after disconnecting the rubber tube or, better, by pulling out the filter plug with a pair of forceps while holding the tube in an almost horizontal position, and expelling the liquid against an object slide by compressing the rubber tube.

Instead of paper, a rolled plug of asbestos or other fibrous material can be employed.

The plug filter has the advantage that little manipulative skill is required in its use and that it is applicable to the filtration of liquids contained in watch-glasses, crucibles, evaporators, etc. But, on the other hand, considerably larger volumes of liquid are required than when using the Behrens-Hemmes method.

Capillary tubes of silica or glass flared funnel shaped at one end ("filter sticks") are also useful. In these the filter may be of paper pulp, asbestos, or other fibrous material. Tiny funnels of glass or fused silica with fritted glass or silica filter septums are carried in stock by dealers in microchemical apparatus.

The authors have found in certain instances that "Alundum" filters have proved of great value. Such filters are made by grinding tiny conical plugs from pieces of broken "Alundum" crucibles and fusing these plugs into the ends of glass tubes 2 to 2.5 mm. in diameter and 50 to 60 mm. long, or plugs of sintered glass can be used. After fusing, exceptional care must be taken in cooling and annealing. In like manner porous porcelain plugs may be used, but in such an event a powerful suction pump is required, suction by means of the mouth being in-

sufficient to cause the passage of the liquid. With care in fusing the glass to the porcelain, tiny germ-proof filters are thus obtained.

An automatic filtering pipette has been devised by Edgeworth-Johnstone,<sup>11</sup> Fig. 9. This is a modification of the capillary filtering tubes of Hemmes, using a small piece of rather thick filter paper. The pipette is applied to the filter paper with the object slide in a horizontal position and advanced together into the drop to be filtered and the object slide at the same time is gradually inclined. The liquid rises in the tube and through siphon action passes over into the small bulb. The pipette can then be lifted off the paper without danger of loss. This device is convenient when dealing with large drops. Unfortunately it is not easily cleaned. In order to function, the capillary bore must be absolutely free from repellent films. Before use it is wise to pass a little alcohol through the tube, expel the alcohol by shaking, warm gently until dry, and use at once.

Centrifugal separation (see *Vol. I*, page 146) is a valuable substitute for filtration, both because of the avoidance of loss of precipitate on the filtering medium and because strongly corrosive liquids, which

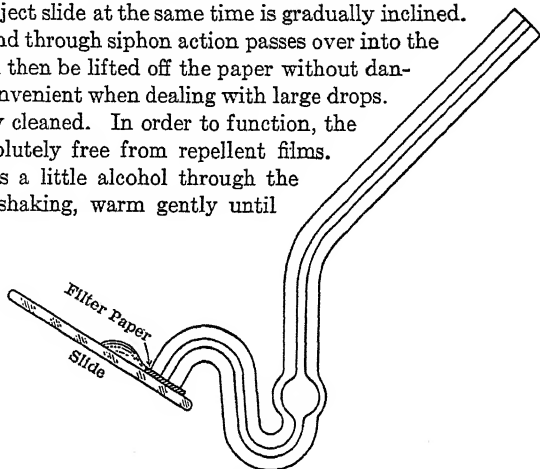


Fig. 9. Edgeworth-Johnstone Automatic Filtration Pipette. Full size.

would attack paper or asbestos, can be handled. By inserting a tiny

filtering tube within a centrifuge tube of ordinary size, centrifugal force may be used as a substitute for suction.<sup>12</sup> The centrifuge is particularly useful in clearing viscous liquids.

**Sublimation.**—The methods and apparatus for separations and analyses by sublimation have been discussed at length in *Vol. I*, pages 343–347. The simplest procedure consists of subliming from one object slide to another.

One form of apparatus

which the authors have found to be especially useful is shown in Fig. 10.

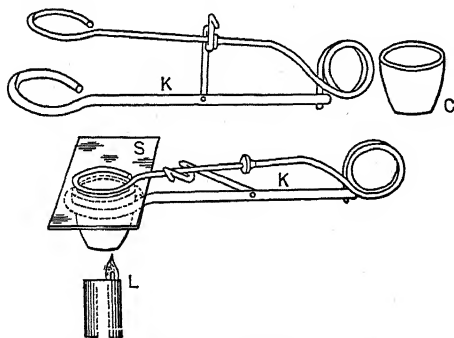


Fig. 10. Apparatus for Microsublimation, Microdistillation, and Gas Evolution. *K*—spring clamp. *C*—glass crucible. *S*—object slide. *L*—micro burner. ( $\frac{1}{2}\times$ )

<sup>11</sup> *J. Soc. Chem. Ind.* 50, 182T (1931).

<sup>12</sup> Emich: *Lehrbuch der Mikrochemie*, p. 47.

It will be frequently referred to in the present volume in the discussion of qualitative tests for both cations and anions.

In inorganic qualitative analysis the sublimation of oxides and chlorides is more conveniently performed by heating on platinum, tantalum, or nickel spatulas (Fig. 22, page 26). The sublimate is collected on silica or "Pyrex" object slides, or if care is used the sublimate can be condensed upon object slides of ordinary glass.

When a very small amount of material is to be handled, sublimation in a drawn-out capillary tube, preferably of hard glass, prevent losses (Fig. 29, page 44).

Difficultly volatile substances, such as metallic oxides, may be sublimed on charcoal or plaster of Paris by means of a blowpipe to give coatings which have characteristic appearances.

**Distillation.** — Fractional as well as simple distillations can be successfully performed on a micro scale and the separations effected are usually sufficiently sharp for the purposes of qualitative analysis.

Fractional distillations with temperature control are, however, rarely practicable on a micro scale. The results obtained do not ordinarily warrant the time and trouble involved in the setting up and the operating of complicated apparatus and the acquiring of the requisite technique.

The microdistillation apparatus and methods which have been described are many and varied.<sup>13</sup> In the present Handbook the authors have confined themselves to a discussion of those methods only which are in use in their laboratories.

For fractional distillation of volatile liquids, small distilling tubes can be employed and satisfactory results obtained. A convenient form is shown in Fig. 11,<sup>14</sup> page 19. To introduce the liquid to be distilled, a rubber pipette cap *r* is slipped over the large end of the tube (Fig. 11 *B*); the tube is inverted as shown and the liquid drawn into the bulb in sufficient volume to fill not quite half of it. The tube is then again turned to the position *A*, the bulb containing the volatile liquid is surrounded by ice (or a freezing mixture), and the drawn-out tube sealed off in the flame of a blast lamp or blowpipe. The bulb is removed from the ice, wiped dry and the apparatus arranged as shown in Fig. 11 *C*. The liquid may now be heated, and the successive fractions which

<sup>13</sup> Behrens-Kley: *Mikrochemische Analyse*.

Emich: *Mikrochemische Praktikum* (1931), p. 33, *Lehrbuch der Mikrochemie* (1926), pp. 56, 123.

Benedetti-Pichler: *Fortschritte der Mikrochemie in den Jahren 1915-1926*, p. 176.

<sup>14</sup> This is essentially a modification of Behrens' double-bulbed tube, but is somewhat more convenient. Emich has described a closely similar modification.



condense, removed with a pipette drawn down to a fine tube having a slightly curved end. (See *Vol. I*, page 142, Fig. 71.)

If the compound is to be distilled must first be set free by the action

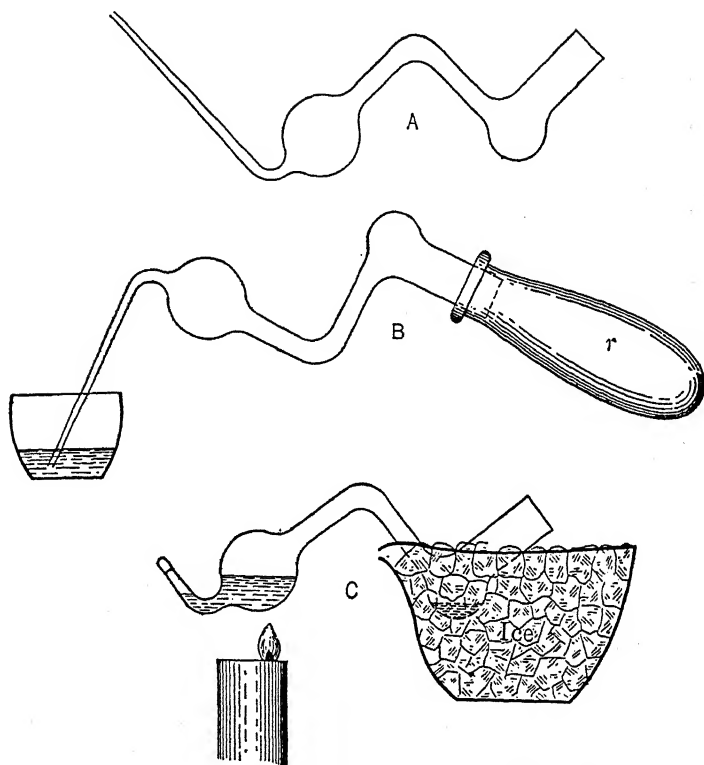


FIG. 11. Fractional Distillation of a Volatile Liquid.

of some reagent, the tube shown in Fig. 12 is to be preferred. Material and reagent are introduced through the side arm, which is then closed with a tiny plug of soft wood or cork, or by fusion. Condensation is obtained by winding the narrow inclined tube with filter paper or cloth wet with cold water or a volatile non-flammable liquid. If the distillate is quite volatile, the receiving bulb should be surrounded by ice, as shown in Fig. 11. When temperatures of vaporization are required, the bulb containing the liquid can be introduced into one of the hot

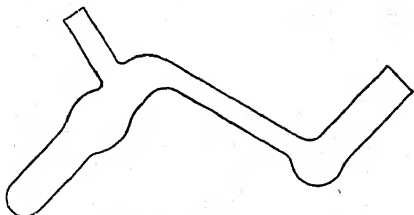


FIG. 12. Tube for Microdistillation.  
(Actual size.)

stages shown in *Vol. I*, Fig. 87, Fig. 89, pages 200, 203, or into an oil bath.

**Distillations involving no fractionations** can be successfully and more conveniently performed in the apparatus shown in Fig. 10, page 17. It consists of a container *C* which may be of glass, quartz, porcelain or metal. The rim of *C* is ground smooth and true so as to fit hermetically against an object slide *S* when in use. The clamp and holder *K* serve to support the container and to hold the cover tightly in place during the heating. To keep the condensing surface cool, a large drop of water can be placed upon the upper surface of the slide within the upper ring of the clamp, or better, a cooled cylinder of silver, aluminum, or copper can be placed within the ring. A cylinder 1 cm. high and of a diameter to fit easily within the upper ring serves as a very efficient cooler, especially if a cup-shaped depression is made in the upper end and in this depression a little chloroform, carbon tetrachloride, or other very volatile non-flammable liquid is placed.<sup>15</sup>

The procedure in a distillation is as follows. Place in the container the material to be treated. Lay over it a tiny bunch of fibrous asbestos which has just been ignited to redness by being held with the forceps in the flame of a Bunsen burner. In the absence of asbestos, pure glass wool or in certain cases even a piece of filter paper may be employed as the absorbent; but, if filter paper is employed, a blank must always be made to prove that no misleading substances result. The asbestos or glass wool prevents the spurting and splashing of the liquid. Upon the absorbent is placed a small amount of the material to be tested. Invert a glass slide over the container thus prepared. Clamp the cover-slide firmly in place, and heat gently over a micro flame until a sufficient condensation has taken place upon the slide. The clamp is then opened by means of the lever and the slide carefully lifted off the container *C*, turned over, and the condensate subjected to such treatment as is required for its identification.

Although the device just described may be applied to the fractional distillation of small amounts of volatile liquids, the distilling tubes described above will be found better adapted to this sort of work.

**Fusions** are performed in depressions made in platinum, silver, or nickel foil or in tiny vessels of metal, silica, or porcelain, or hemi-

<sup>15</sup> Conversely, when subliming compounds with a high subliming point, it is often advisable to keep the object slide warm in order to induce the formation of larger and better crystals. Gas-carbon or graphite cylinders, previously warmed, hold their heat for a sufficient period to enable the analyst to obtain excellent sublimates upon the cover-slide, (*e.g.*,  $\text{As}_2\text{O}_3$ ).

spherical depressions are hollowed out in a block of carbon or graphite and material fused therein by means of a blowpipe.

Satisfactory cups for very small amounts of material can be readily stamped in thin platinum foil. A brass or bronze rod is shaped to conform with the size and style of cup desired; it is then hammered into a block of lead. This gives a die by which tiny cups can be rapidly and inexpensively made. Figure 13 shows block, plunger, and cups of different depths. It is convenient to prepare a block of lead with depressions of different depths, thus providing for fusions of varying amounts of material. After the fusion has been completed, the fused mass removed, and the "cup" cleaned, it can be reshaped by laying it in the dye and giving it a slight tap with the plunger and a small hammer. For larger amounts of material the platinum cups shown in Fig. 14 will prove useful.

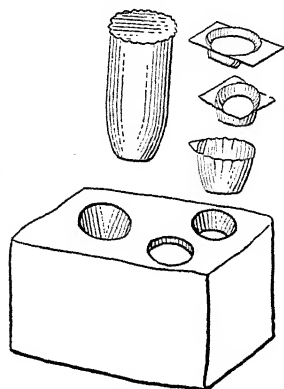


Fig. 13. Block and Plunger for making Foil Cups.

Similar tiny, shallow, platinum cups can be made by pressing the foil upon soft rubber, using glass rods with rounded ends.



Fig. 14. Platinum Cups for Fusions. (Full size.)

All cups or foils are handled by means of forceps, but, when blowpipe fusions must be practiced, compression forceps of the type shown in Fig. 15, page 22, are a great convenience, because they can be locked shut, thus relieving strain on the fingers during a long fusion, and eliminating the danger of dropping the bits of foil or tiny cups.

For blowpipe fusions, the Grunberg Orthodontic Blowpipe (Fig. 16, page 22) will be found exceptionally convenient. This model is not adapted for use with natural gas.

Fusions at Bunsen burner temperatures are made over burners of the type shown in Fig. 1, page 5. The platinum wire triangle in the ring A can be readily bent so as to support the cups shown in Figs. 13, 14.

The fusing mixture is placed in the "cup," heated slowly, and the temperature raised until it has been brought to complete fusion. The melt is then removed from the flame and a tiny fraction of the material

under investigation is added. The preparation is then heated to complete fusion, a second portion is added, and the process kept up until sufficient material has been added to meet the requirements of the analyst. In the great majority of cases this fractional addition is preferable to adding the whole amount at once, for the progress of the reaction is more readily followed.

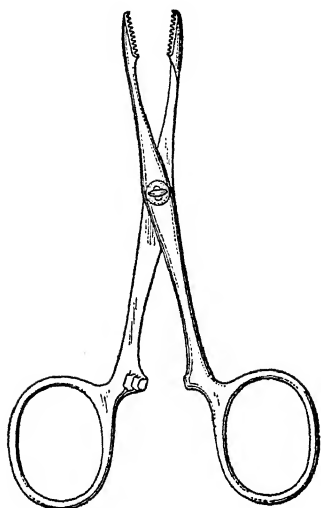


FIG. 15. Surgical Compression Forceps. Convenient for Holding Small Cups or Pieces of Foil.

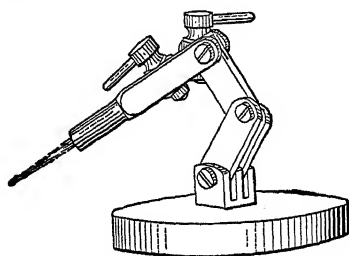


FIG. 16. Grunberg Orthodontic Blowpipe  $\times \frac{1}{2}$ . (S. S. White Dental Co.)

Fusions with  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$  are best made in platinum, those with  $\text{NaOH}$ ,  $\text{KOH}$ , and  $\text{Na}_2\text{O}_2$  in silver, those with  $\text{KOH}$  and  $\text{KClO}_3$  in porcelain. Metals and alloys can be fused on carbon, using a suitable flux to prevent oxidation.

Very small amounts of material may conveniently be subjected to fusion in a bead contained in a platinum loop. A blast lamp of the type shown in Fig. 16, or a mouth blowpipe may be used, with either an oxidizing or a reducing flame. Color reactions in the melt, and suspended or skeletal material in the bead, may be observed as guides to chemical testing.<sup>16</sup> Borax, or "microcosmic salt" ( $\text{HNaNH}_4\text{PO}_4 \cdot 4 \text{H}_2\text{O}$ ) are the most commonly used fluxes. The platinum loop can easily be cleaned by breaking off the bead, and then by "rinsing" with successive beads of fresh flux.

The platinum loop can be heated to the proper temperature for fusing the bead by passing an electric current through the wire (R. N. Titus), thus bringing about a fusion without contact with gas combustion products.

**Ignitions** are performed in the manner usually employed in quantitative work, but to avoid possible losses through convection currents it is better to carry out

<sup>16</sup> Moses and Parsons: *Mineralogy, Crystallography, and Blowpipe Analysis*. Kraus and Hunt: *Mineralogy* (1928), Chap. XV.

the heating in some type of muffle which may be either gas or electrically heated. Figure 17, illustrates a type of tiny muffle furnace that is easily made of hard glass (or better of fused silica) and will be found practical and efficient.<sup>17</sup>

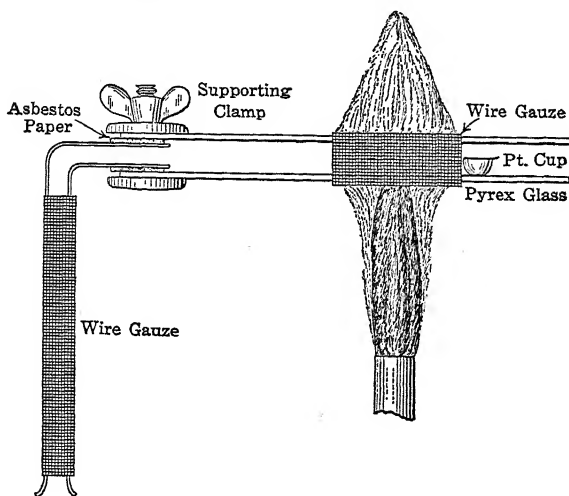


FIG. 17. Pregl Type Muffle for Microignition.

**Reagents and Their Application.**—Since the reactions employed in microscopical qualitative analysis are extraordinarily sensitive, unusual care must be taken to avoid contamination of reagents. Liquids and solutions kept in small bottles for convenient use should be frequently renewed, since they soon become contaminated by foreign material derived from the containers. As many reagents as possible should be kept in the solid state rather than in solution. One of the most serious sources of contamination is “dust” from the air falling about the stopper of the bottle and finding entrance into its contents whenever the stopper is removed.

Acids, distilled water, and solutions in constant use are conveniently kept in bottles of the type shown in Fig. 18.

A practical and wholly satisfactory system for reagents frequently required in qualitative analysis is that due to Behrens (Fig. 19, page 24). It consists of a box housing 60 or more 1 cc. glass-stoppered vials. When not in use the cover protects them

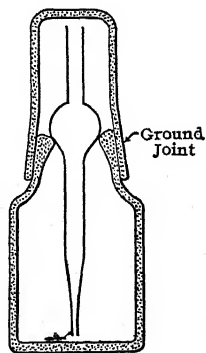


FIG. 18. Dropping Bottle with Pipette and Cap.  $\times \frac{1}{2}$ .

<sup>17</sup> Pregl-Fyleman: *Quantitative Organic Microanalysis*, p. 165 (1930).

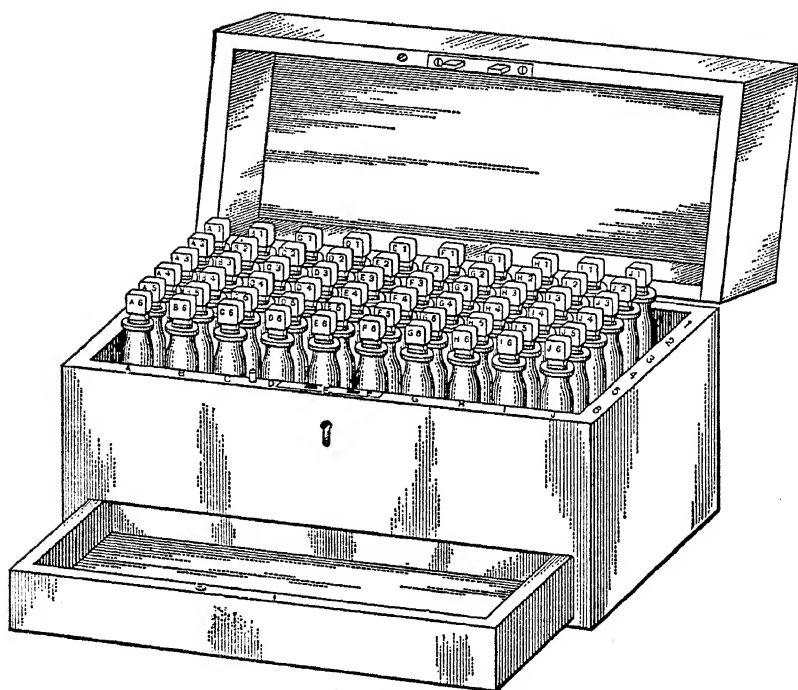


FIG. 19. Reagent Set for Microchemical Analysis. (Behrens.)

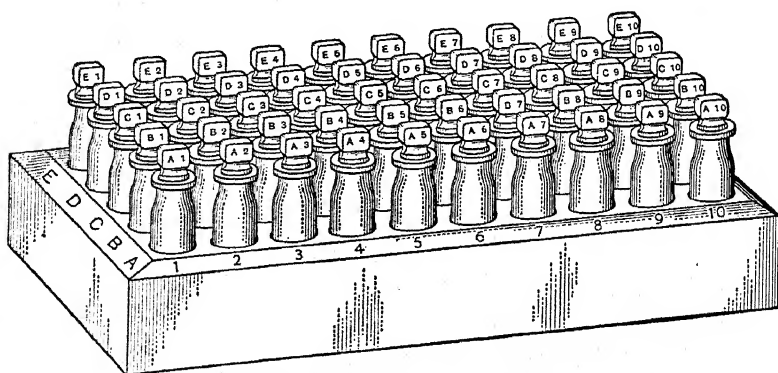


FIG. 20. Wooden Block with Small Vials for Reagents.

from dust and dirt. Or we may use a simple block to hold the vials (Fig. 20).<sup>18</sup> A chart giving a list of the reagents required in the routine analysis of common inorganic compounds will be found on page 428.

A number of reagents, even in the comparatively dry state in which they are placed in the vials, attack the glass and become seriously contaminated. An excellent example is afforded by uranyl acetate. This salt takes up sufficient sodium in a short time to render it unfit for use. To prevent this deterioration, the vials can receive a coating of ceresin or other suitable wax, or a coating of varnish, or a small cylinder of paper with twisted end can be inserted in the vials.

Ammonium bifluoride can be kept in tightly stoppered ebonite tubes as shown in Fig. 21, or the tubes can be fitted with ordinary soft rubber stoppers. Ammonium bifluoride of commerce is unfit for microanalyses unless it has been carefully re-sublimed in platinum. This can be done by heating in a platinum dish and condensing the vapors upon the under side of another platinum dish filled with cold water. The operation must be conducted in a hood.

All reagents should be tested for their purity by performing "blank" tests. In this connection it must not be forgotten that practically all the rubber goods of commerce contain a considerable quantity of "filler" which is readily soluble in acids and other liquids. It is therefore important that contact of reagents with rubber should be avoided as much as possible. The most frequent cause of trouble is zinc in the reagents derived from the zinc oxide used as a filler; red rubber often contains antimony sulphide.

Reagents can be handled by means of drawn-out glass rods, or platinum or tantalum wires fused into a glass handle (Fig. 22). If about 1 mm. of the very tip of the rod is slightly roughened with HF or by rubbing with a piece of abrasive cloth or paper, it will pick up

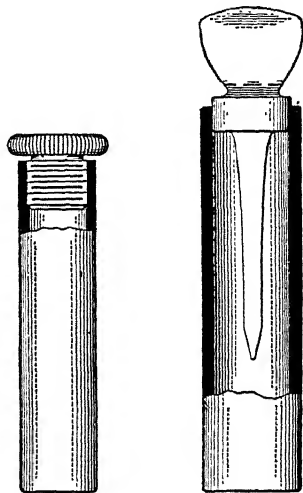


FIG. 21. Ebonite Tubes for Ammonium Fluoride. (Behrens.)

<sup>18</sup>Such a set of reagents can be obtained from R. P. Cargille, 118 Liberty St., New York City, the Will Corporation, Rochester, N. Y., Eimer & Amend, New York City, and Fisher Scientific Co., Pittsburgh, Pa.

Small reagent vials with screw tops and molded plastic caps can be obtained in sets from R. P. Cargille, 118 Liberty St., New York City, and from Fisher Scientific Co., Pittsburgh, Pa.

both solids and liquids better. To pick up solids, the end of the tube or wire is breathed upon and then immediately applied to the powdered material; several particles will adhere and can be transferred to the drop to be tested. Simply dipping into a liquid and withdrawing without touching the neck of the container will ensure that a drop of the liquid will cling to the glass or wire.



FIG. 22. Drawn-out Glass Rod and Platinum Wire for Handling Reagents.

Glass rods drawn out to a diameter of a little less than one millimeter and cut into lengths of about 70 mm. will be found very convenient for transferring material. After being once used, they may be thrown away, thus avoiding possible contamination through inadequate cleaning of rods. In like manner fine capillary tubes may be prepared from odds and ends of glass tubing to serve as pipettes, and after using are rejected.

For transferring larger amounts of material, a small platinum spatula is indispensable (Fig. 23). It is made from a piece of hard, drawn



FIG. 23. Platinum Spatula. (Full size.)

platinum wire about 1 mm. in diameter and 80 to 85 mm. long; one end is hammered flat upon a polished steel surface until it becomes a little over 3 mm. wide and the flattened surface about 10 mm. long. The blade is then shaped with a file, smoothed, and polished. The opposite end of the wire is given a blow or two of the hammer and filed to a double chisel edge and polished. This end is used chiefly for loosening reagents in vials and for breaking up fragments of soft or friable salts.

It is often necessary to screen small amounts of material. This can be accomplished by means of silk bolting cloth of suitable mesh size. The cloth is stretched in a tiny metal frame constructed upon the principle of embroidery rings, as shown in Fig. 24. After use, the cloth is removed and thrown away.<sup>19</sup>

The various methods for applying reagents are discussed in detail in Chapter II.

In all discussion of tests in this Handbook the authors have made use of certain terms which need a few words of explanation.

<sup>19</sup> Standard sieves three inches in diameter are carried in stock by the Newark Wire Cloth Co., Newark, N. J. Smaller sizes can be obtained on order.



**Test Drop.**—The drop of solution containing the material to be tested. Unless otherwise specified, this drop is supposed to be spread out upon the object slide over a circular area about 6 to 7 mm. in diameter and to be not over 1 mm. deep at its center. Smaller drops may be used if desired, but they are likely to be so highly curved as to prevent observation of precipitates within them; or they may spread out upon the slide in so thin a layer that evaporation at room temperatures may be too rapid to permit the formation of characteristic crystals.

**Reagent Drop.**—The solution of the reagent. If this drop is placed upon the object slide and caused to flow into the test drop, it should not be spread out in a thin layer but should be almost twice as deep as the test drop.

**Inner Zone of Precipitate.**—The relative position shown at *i* in Fig. 25.

**Outer Zone of Precipitate.**—The relative position shown at *o* in Fig. 25.

**Concentrations** are in general discussed in terms of the *size* of the fragments of unknown and reagent and may be indicated thus, for substances readily soluble in water (the test drop being 7 mm. in diameter and 1 mm. deep):

- |                                     |                                     |
|-------------------------------------|-------------------------------------|
| 1. <i>Very dilute</i> ,             | a fragment the size of this dot (.) |
| 2. <i>Dilute</i> ,                  | " " " " (•)                         |
| 3. <i>Moderately concentrated</i> , | " " " " (•)                         |
| 4. <i>Concentrated</i> ,            | " " " " (•)                         |
| 5. <i>Very concentrated</i> ,       | a practically saturated solution.   |

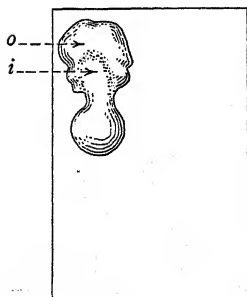


FIG. 25.

It will be obvious that any such arbitrary designations of concentrations cannot be applied to difficultly soluble compounds, and can serve merely as a rough guide of relative values. These designations have been used because of the criticism that has not infrequently been made that authors of microchemical tests use the terms *concentrated* and *dilute* with no explicit statements. Per cent concentrations are impractical since it is impossible to estimate weights and volumes when dealing with such small quantities, and when dealing with unknown materials and mixtures there is no knowledge as to compositions.

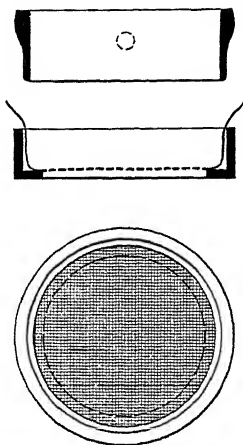


FIG. 24. Sieve of Silk Bolting Cloth. (Full size.)

**Sensitivity of Reactions.**—It is perhaps unfortunate that in the past so much stress has been laid upon the sensitivity of microscopical chemical tests, both because their advantages of ease and directness are thereby obscured, and because the impression is given that they are appropriate only in case extremely minute amounts of material or low concentrations are to be dealt with. Actually, of course, a chemical reaction involving the formation of a precipitate will give a positive result whenever the "solubility product" of the precipitate is exceeded, whether the reaction is carried out in a drop or in a test-tube. Since the great majority of reactions used in microscopical analysis are also employed in ordinary macroscopic analysis, it is evident that, in terms of concentrations of the reacting solutions, no increased sensitivity can result. Furthermore, these reactions are usually at a distinct disadvantage when applied as microscopical tests, and in most cases are unsatisfactory at dilutions distinctly less than those which correspond to the solubility of the precipitate. This is due to the fact that the *effective* "solubility product" of a given precipitate may vary greatly, depending upon the presence of other ions (not necessarily "common ions") and the formation of complex ions. In addition it must be borne in mind that macroscopic tests are ordinarily carried out in solutions which have been subjected to preliminary separations, whereas microscopical tests are usually made in the presence of whatever other substances happen to be in the unknown solution.

The factors which often govern the choice of a reagent for microscopical tests may be directly at variance with the chief considerations in macroscopic tests. Definitely crystalline precipitates are sought in microscopical analyses in order that their form and optical properties may serve to identify them. Distinctive crystals are not ordinarily obtainable by the precipitation of highly insoluble substances such as those on which most macroscopic tests are based. Consequently there is frequently a deliberate sacrifice of sensitivity, by the choice of a reagent which will give a relatively soluble precipitate in recognizably crystalline form, instead of one which will yield an apparently amorphous precipitate at extreme dilutions. The use of  $\text{Ca}^{++}$  instead of  $\text{Ba}^{++}$  in testing for  $\text{SO}_4^{--}$  is a good example of this. Occasionally the conditions under which the test is made are purposely altered in the direction of a reduction of sensitivity, so as to obtain a more characteristic precipitate; for example, in the precipitation of  $\text{Ag}_2\text{CrO}_4$  or  $\text{PbI}_2$  from slightly acid solution.

The apparent sensitivity of microscopical qualitative reactions is increased by a number of factors. The material to be tested appears, in the solid state, to be exceedingly minute. It must be remembered that the solvent is used in correspondingly minute quantity, so that actually the solution may be fairly concentrated. The reagent, especially when added as a solid, is commonly present in concentrations which may approach saturation. A drop of the unknown solution, too dilute to give an immediate precipitate, may yield crystals on standing or warming, due to evaporation and concentration of the solution.

The influence of the various factors mentioned above renders any numerical expression of the sensitivity of a reaction of somewhat questionable value, since it may be subject to so many influences. As a means of indicating roughly the relative limits of different tests, such data may be useful, but a negative test should never be interpreted as indicating that the actual concentrations or quantities of the material sought are less than the reported sensitivity.

Sensitivities of reactions may be expressed in various ways:

1. As the limiting concentration, in grams per liter or cubic centimeter, or  $\mu\text{g.}^{20}$  per drop of definite volume, at which a definite positive test is obtained.
2. As the minimum amount of material which will yield a positive test.
3. As the minimum percentage of material, in the presence of another material, from which a positive test may be obtained at a given dilution.

The first method of stating sensitivities will, of course, be related to the second, if the amount of solution employed is known. This may range from several drops (say 0.2 cc.) to one drop (ordinarily about 0.02 cc.). If the solution to be tested is concentrated further, before the test is applied, the limiting concentration in the original solution may be very much less than if this solution were tested directly. The advantage of such procedure, when several drops of a highly dilute solution are available, is obvious, but a "blank" should be run to eliminate the effect of an impure solvent. The limits of sensitivity should also, if possible, be stated for different mixtures of materials, especially in cases where the test is commonly employed to detect small amounts of one substance in the presence of another.<sup>21</sup>

**Character of Precipitates.**—A precipitate has been designated as "amorphous" when a magnification of 200 to 300 $\times$  fails to disclose any fine crystals, but merely flocs or curdy or gelatinous masses; it has been called granular when it consists of dispersed particles so fine as to appear as dots only; if these dots can be resolved into more or less spherical grains under a magnification of 150 or 200 $\times$ , the precipitate has been called sandy or as consisting of granules.

The photomicrographs illustrating the various tests are roughly representative of the size of the crystals obtained, at the magnifications indicated. However, since the fineness of a precipitate can vary over wide limits, depending on the concentrations of the reacting substances, temperature, digestion, etc., the dimensions of crystals cannot be used as a positive criterion for differentiating between substances having similar form.

<sup>20</sup> 1  $\mu\text{g.}$  (microgram = 0.001 mg. = 1  $\gamma$  (gamma). 1  $\lambda$  = 0.001 ml. = ca. 1 mm<sup>3</sup>.

<sup>21</sup> Discussions of the sensitivity of microscopical reactions, and methods of expressing it, are given by:

Behrens-Kley: *Mikrochemische Analyse* (1921), p. 3.

Feigl: *Mikrochemie* 1, 4 (1923).

Emich: *Lehrbuch der Mikrochemie* (1926), pp. 3, 7.

Hahn: *Mikrochemie* 8, 75 (1930); 10, 313 (1931).

Heller: *ibid.* 8, 141 (1930).

## CHAPTER II

### METHODS OF APPLYING REAGENTS IN MICROSCOPICAL QUALITATIVE CHEMICAL ANALYSIS

In order that characteristic tests which are always dependable and readily interpreted may be obtained, it is essential that the analyst shall bring about a given reaction under definite and reproducible conditions.

Most of the "micro" tests available for the detection of ions, complexes, or compounds are dependent upon the separation of a crystalline phase which possesses a constant crystal habit peculiar to the substance being sought.<sup>1</sup>

To bring about the proper conditions which shall ensure a rapid and certain reaction requires that a given test shall be performed always in the same manner and under the same conditions, for we require not only a definite reaction product but also one which shall separate always with the same crystal habit, and form crystals of approximately the same size whenever the test is made.

The necessity of controlling the conditions under which the reaction product is formed will be even more obvious if it is recalled that many compounds exist in two or more forms. Some of these forms are unsatisfactory as reaction products upon which to base an opinion, and it is necessary so to perform a test as to ensure the separation of the proper phase.

Under similar conditions as to concentration of substance and reagent, acidity or alkalinity, temperature and manner of reagent application, the crystalline phase will not only separate with always the same habit, but the majority of the crystals will usually develop to the same size and will lie on the same faces upon the object slide, in each separate experiment.

In order that a test may prove satisfactory and conclusive, the solid crystalline phase desired should separate almost immediately. If long in forming, evaporation takes place and it is highly probable that other crystalline compounds may then separate and thus mask the test. On the other hand, conditions leading to the instantaneous precipitation of the identifying reaction product usually force it to separate in such a

<sup>1</sup> See *Vol. I*, Chap. X, p. 327.

finely dispersed state, or in such non-characteristic skeletal forms, as to render the test of questionable value.

However, when skeletal crystals can be obtained which are more specific, or more readily formed, or are larger than the normal crystals, it is better practice to control the conditions in the test drops so as to induce the formation of the more easily identified malformed crystals, *e.g.*, the detection of Zn, Sr, Ba, As, Mg, and many reactions with organic reagents.

**Method I:** A drop of a solution of the reagent is caused to flow into a drop of the solution of the material to be tested. — This method of adding the reagent to the test drop is of general applicability and can be employed in practically all "micro" tests made upon object slides. By its use the quantity of reagent brought into reaction with the unknown ions is more readily controlled than is possible by other methods, and there are fewer complications in the interpretation of the phenomena produced.

Preliminary tests with a given reagent are best made by this method, and from the results obtained the most satisfactory method of reagent application can be properly judged.

Near the corner of a scrupulously clean slide (see page 11), place a drop of a solution of the material to be tested. Spread the drop with a glass rod or platinum wire until it attains a diameter of about 5 to 7 mm. and a depth of less than 1 mm. This drop will hereafter be called the test drop.

A drop of the reagent solution of a diameter of approximately 5 mm. is next placed close to the test drop, but not touching it. The concentration of the reagent drop should (save in very exceptional cases) be slightly greater than that in the test drop, or, to be more exact, the density of the reagent drop should be sufficiently greater than that of the test drop to ensure the reagent solution sinking into the liquid of the test drop.

By means of a drawn-out glass rod, or by means of a platinum wire, a tiny channel is made to flow from the reagent drop into the test drop, the object slide being tipped very slightly to facilitate the flow; but under no condition should the two drops merge. Care should be observed, when introducing the reagent into the test drop, not to rub the glass slide with rod or wire; otherwise too rapid crystallization may result.

Crystals formed upon the slide have their more perfectly developed faces on the upper side and can be more easily studied. Floating crystals, supported by surface tension, grow downward into the liquid and as they grow and become heavier they tend to sink deeper; the upper

side alone can be studied, and as this is always irregular, malformed, and seldom transparent, the true habit of the crystals may not be distinguishable or may be misinterpreted.

When the reagent is properly added, the preparation should appear as shown in Fig. 25, page 27.

As the reagent enters the test drop, the formation of the reaction product creates a dam or hinders the direct flow of the reagent solution, the velocity of the further reaction is checked, and, at some point where the channel enters the test drop, concentration conditions will exist favorable for the growth of well-formed characteristic crystals of the product sought. This favorable condition may be in the outer zone *o* or in the inner zone *i*.

In very rare cases better results appear to be obtained by causing the solution of the substance to be tested to flow into the reagent drop.

*Typical Applications:*

See Potassium, Method A, page 65.

Zinc, Method A, page 136.

**Method IA:** A drop of the reagent is caused to flow into the test drop which has been covered with a cover-glass. — When a reaction product has an exceptionally low solubility and therefore an almost instantaneous precipitation results, the crystals formed have a tendency to be more or less malformed and atypical. A high power is required for their resolution. Unless the objective employed is one which has been constructed for the examination of uncovered objects, a cover-glass is essential. Under these conditions it is often more satisfactory to introduce the reagent into the test drop very slowly in the following manner. A drop of the solution to be tested is spread upon the object slide; a glass hair or a fragment of a No. 1 cover-glass is placed close to the drop and a *clean* cover-glass carefully lowered upon it, avoiding the introduction of air bubbles, and so placed that one edge of the cover rests upon the hair. The drop should not fill completely the space between cover and slide. The reagent is applied to the thicker or open end of the preparation in a more concentrated form than in common practice. The preparation should stand undisturbed for several minutes before being examined.

If the preparation is to be photographed, this procedure is invaluable since it almost completely eliminates free-swimming crystals and ensures well-developed characteristic crystals.

Metastable conditions can be upset by gently pushing the cover-glass a very little.

**Method IB:** A drop of the reagent is added directly to the test drop at its center. — This method is applicable to all reactions not requiring careful control of concentrations, or, in other words, tests in which the reaction product will invariably separate under wide variations of conditions.

The usefulness of the method is usually restricted to adjustment of acidity or alkalinity; to precipitations where the crystal form is imma-

terial and a solid phase is produced for the purpose of separating it from other compounds, in order that tests of some sort may be subsequently applied to it, or to the solution from which it has been eliminated. It is also successful where a solution of exact strength is added to a test drop of known concentration. In all other cases Method I is to be preferred.

**Method IC: Reactions in capillary tubes.**—Reactions can be carried out in capillary tubes, the resulting precipitate being observed under the microscope. Glass tubing, carefully cleaned and drawn out to about 2-mm. inside diameter, is cut and sealed off to give lengths which are used just as are test-tubes.<sup>2</sup>

Volatile liquids can be handled with little loss, and warming or digestion can be carried out with less evaporation than from a drop on an object slide.

For transferring liquid from one capillary tube to another, and for separating precipitates, the centrifuge is convenient. Pipettes made from tubing drawn down to 1-mm. or less outside diameter are useful for drawing off supernatant liquids, collecting sediments, introducing reagents, etc.

**Method II: A fragment of the solid reagent is added to a drop of the solution to be tested.**—This method is designed to ensure the presence of an excess of the reagent at the very beginning and during the early progress of the reaction. It is of special value when the reaction product is a double salt in which the reagent must be present in the greater ratio, or when two double salts are possible (e.g.,  $3 \text{ CsCl} \cdot 2 \text{ BiCl}_3$  and  $3 \text{ CsCl} \cdot \text{BiCl}_3$ ) and it is the salt with the larger proportion of reagent that is desired; in such cases a large fragment of the reagent is added at the center of the shallow test drop. The preparation must not be stirred.

The size of the reagent fragment should be such that its upper surface shall be at the surface of the drop, or better, just barely above it. The reagent dissolves at a very high concentration, and sinking into the less concentrated test drop causes convection currents to bring the material to be tested in contact with an almost saturated solution of the reagent. When, however, a great excess of the reagent is to be avoided, the fragment introduced into the drop should be very small. Except as a matter

<sup>2</sup> Fuchs: *Monatshefte* 43, 129 (1922).

Emich: *Mikrochemisches Praktikum*, 2 Auf. (1931), p. 25.

*Lehrbuch der Mikrochemie* (1926), p. 44.

Hahn: *Emich-Festschrift, Mikrochemie* (1930), p. 143.

As an illustration of this technique, see Benedetti-Pichler: *Ind. Eng. Chem. (Anal. Ed.)* 2, 309 (1930).

of convenience, Method II will be found to be less useful in general than Method I.

It not infrequently happens that in the disintegration and solution of the reagent fragment, a saturated solution of the reagent results in a zone about the fragment, and as a consequence crystallization of the reagent itself takes place. The inexperienced analyst may thus be misled and mistake these crystals for a compound formed by the reagent with some salt present in the test drop. This source of error can be avoided if the crystal habit of the reagent has been previously studied. Another puzzling phenomenon, occasionally observed, is that of the temporary formation of a compound in a zone in contact with the reagent fragment, and the almost instantaneous disappearance of the crystals as they drift beyond the zone of high concentration. Hydration of dehydrated reagents, or the decomposition of one which is a double salt (for instance,  $\text{K}_2\text{Hg}(\text{SCN})_4$ ), may result in such apparent anomalies.

Method II is unsuited to reactions in which the reaction product is very difficultly soluble or is curdy or flocculent, for under such conditions the reagent fragment becomes immediately coated with an almost impenetrable phase and the reagent cannot dissolve and enter into a further reaction. Under conditions such as these Methods I or IB must be resorted to.

Method II will be found a safe procedure in most reactions where the reaction product first formed is soluble in excess of the reagent, for the analyst wishes to see the solid phase formed by the reaction and also observe its solubility in an excess of the reagent.

Adding the solid reagent provides for both precipitation and subsequent re-solution. There is always an appreciable time, owing to the slow solution of the reagent, during which there exists a zone where the concentrations are such that the solid phase of the reaction product can exist. Thus the fragment of the reagent will be surrounded by a clear ring or zone at the outer edge of which the solid crystalline phase may be easily seen under the microscope. If the fragment of the reagent is too large or dissolves too quickly, the zone of solution may increase so rapidly that it reaches the circumference of the test drop before the analyst has time to note the formation of the transitory solid reaction product.

The fragments of the solid reagent added should always be dense and compact, so as to insure its gradual solution; for if it is in fine powder and of such loose texture that it disintegrates, it will dissolve almost instantly when added to the test drop. The conditions then become substantially equivalent to those in Method IB.



If the reagent is available in fine powder only or in a loosely textured condition, it should be fused if such a procedure is permissible, or a portion can be moistened with water and rapidly evaporated to dryness. From the crusts thus formed, compact fragments may be selected.

Just as in Method I, better results may sometimes be obtained if the substance to be tested is added to the reagent; in this case the solid substance is added to the reagent drop. This procedure is limited to a few very special tests. The best example is that of the bismuth sulphate test for the alkali metals.

The addition of the reagent as a solid rather than in solution is also advantageous in reactions resulting in the precipitation of a compound in which the reagent does not enter into combination; as, for example, the precipitation of a compound by the introduction of a like ion, or simply by increasing the concentration of salts in solution.

*Typical Applications:*

See Sodium, Method B, page 58.

Bismuth and Antimony, Method B, page 232.

Electropotential Series, page 401.

**Method III:** The reagent solution is drawn in a narrow channel across a dry film, obtained by evaporating to dryness a solution of the substance to be tested. — There are a few identity tests which give far better and more rapid results if performed in this manner than when the reagents are applied by Methods I or II.

Residues for reactions performed by Method III should consist of thin films in which the material to be tested is distributed uniformly over a circular area about 7 mm. in diameter. Such films are obtained by gentle evaporation. Place a drop of the material to be tested at the corner of a scrupulously clean slide; spread it out in a thin drop not less than 7 mm. in diameter. Warm the preparation and blow gently upon it to hasten evaporation to the saturation point. Reheat and again blow. Spread the drop to a film if necessary, and continue blowing on the heated preparation until the liquid has evaporated, leaving a thin, uniform, perfectly dry film. Care must be observed that at no time shall the temperature be raised to the boiling point, and that the residue is not heated after it becomes dry. Unless these precautions are observed, the residue will not adhere to the object slide; and, when the reagent is drawn across, the dry material will be loosened and the whole area flooded.

Tipping the object slide and heating nearer the center of the slide than the drop will prevent the liquid from creeping and spreading over too great an area.

In case a film is obtained surrounded by a ridge of solid material

coarsely crystalline in character, it is advisable to remove this ridge by means of a tiny spatula, using it shovel-wise.

Sufficient reagent is dissolved in a drop of water to produce an almost saturated or fully saturated solution. This drop should be placed about 3 mm. (not more) from the dry film and drawn across the dry film with a quick stroke of a glass rod or a platinum wire, care being taken to avoid rubbing the glass in leading the reagent across. The preparation should have the appearance shown in Fig. 26.

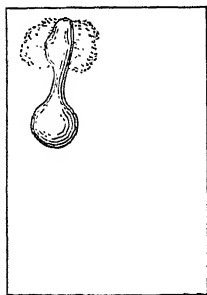


FIG. 26.

The reagent should never spread over the entire film but should remain as a narrow streak of liquid across the film of dry material. Under these conditions the substance subjected to the reaction dissolves in a minimum of solution saturated with the reagent. If an element, salt, or compound is present, capable of forming a product of moderate insolubility, such a reaction product will separate almost at once, even if its solubility is not very low.

To insure the growth of crystals of suitable size for easy detection the slide should be slightly inclined after drawing the streak across, and held very slightly inclined for a few seconds before placing the object slide upon the stage of the microscope.

When the reagent flows over so as completely to cover the film of substance it is usually due to one or more of several causes: too thick a film; too large a glass rod; an object slide that is not clean; heating after the film has become dry and so detaching the crystals from the glass; too much reagent; the presence of excessively soluble or deliquescent compounds that do not remain dry or refuse to cling to the glass slide.

*Typical Applications:*

See Sodium, Method A, page 51.

Potassium, Method D, page 72.

**Method IIIA:**<sup>3</sup> The reagent solution is applied directly to a moist film obtained by evaporating to almost complete dryness a drop of the solution to be tested. — The preparation of the film to be tested is as described under Method III, but the evaporation is conducted at a lower temperature and is checked by cooling the slide before dryness is reached. The reagent drop is then applied in sufficient amount to cover the area of the film in a very thin layer.

*Typical Applications:*

See Nickel, Method A, page 274.

Arsenic, Method B, page 224.

<sup>3</sup> Short: *Bull.* 825, *U. S. Geol. Surv.* 125 (1931).

Method IV: Upon failure to obtain a decisive test, owing to an insufficiently high concentration of the test drop, a separation of characteristic crystals can be obtained through the addition of another ion which will form a less soluble salt of the same nature. — Method IV is based upon the formation of a series of isomorphous compounds of decreasing solubilities. It is of value when the test drop is highly concentrated and evaporation will be followed by the separation of such a large amount of crystalline salts as possibly to mask the test for the ion sought. Time is saved and the apparent sensitivity of the reaction is increased.

An excellent example of this method is to be found in the testing for lead or for copper, by the triple nitrite method. Copper acetate or lead acetate and potassium nitrite are added to the acidified test drop. A triple nitrite of  $\text{Pb}^{++}$ ,  $\text{Cu}^{++}$ , and  $\text{K}^+$  is formed, and separates in tiny black cubes if the concentration is above a certain minimum. Suppose that after the reagents have been applied, no black cubes appear. A salt of cesium or of thallium can be added, for the cesium triple nitrite is less soluble than that of potassium and the thallium salt less soluble than that of cesium. The addition of  $\text{Cs}^+$  or  $\text{Tl}^+$  may therefore cause an immediate separation of the triple salt, and the sensitivity of the reaction in this particular concentration of  $\text{Pb}^{++}$  or  $\text{Cu}^{++}$  has been increased; but if we had allowed the original preparation to pass to dryness we probably would have detected neither  $\text{Pb}^{++}$  nor  $\text{Cu}^{++}$ , because the reaction would have been masked by the large amount of crystalline residue always present in this test.

Tests based upon Method IV are among the most interesting and instructive with which the analyst has to deal. To apply and interpret them intelligently, or to devise new tests based upon this principle, requires a good practical knowledge of the Periodic System.

Assuming that Method IB has been employed and that no reaction product has appeared, there is introduced (Method II) a solid fragment of a reagent forming a salt isomorphous with the reaction product first sought; by this addition the formation of a new and much less soluble phase has been facilitated.

Whenever there exists an isomorphous series of salts of decreasing solubility with increase or decrease of the atomic weight (or molecular weight) of the cation, one cation may be substituted for another, or two or more may be introduced into the same test drop.

*Typical Applications:*

See Potassium, Method A, page 65.

Lead, Method C, page 207.

**Method V:** The reagent is dissolved in alcohol and applied to the test drop or test film. — Alcoholic solutions of reagents or solutions of reagents in other liquids in whose surface tensions are very different from that of water require a special technique, if satisfactory results are to be obtained.

If one attempts to apply a drop of an alcoholic solution to an aqueous drop, it is probable that reagent drop and test drop will flow all over the object slide, that the alcohol will forthwith disappear, and that there will remain a multitude of water droplets scattered here and there upon the surface of the object slide. Water and alcohol are perfectly miscible in all proportions, but the physical reaction resulting from the mixing of two drops whose liquids have very different surface tensions prevents the general use of alcoholic solutions in microscopical qualitative analysis.

When an alcoholic reagent must be added to a test drop or when it is desired to add alcohol alone to a test drop, the aqueous solution should always be placed at the corner of the object slide. Tip the slide before applying the alcohol and, just as the alcohol leaves the glass rod or pipette, increases the inclination of the slide, and as far as possible allow the alcohol to flow upon the slide a *very little* at a time. Be ready to counteract the tendency of the alcohol to creep, by increasing the inclination of the slide to an almost vertical position.

Whenever possible, prepare a dry film of the material to be tested, and cause the alcoholic reagent to flow over the film (Method IIIA, page 36). Hold the slide inclined a few seconds, in order that the reaction may have had time to take place.

Since alcohol has a tendency to flow over the edges of the slide, it is best to lay the slide upon a larger slide, with the corner occupied by the liquid projecting beyond the larger slide. This precaution is taken to prevent the mixture from flowing over the stage of the microscope.

If the non-aqueous liquid creeps to a marked degree, a bit of "Plasticine" or paraffin can be placed upon a larger slide and the object slide held in an inclined position while being examined under the microscope. When this preventive measure is employed, a low-power objective must be used and steps taken to induce the reaction product to acquire reasonably large dimensions.

Reactions involving the use of alcoholic reagents, or precipitations produced by the introduction of alcohol, can often be more conveniently performed in shallow watch-glasses, object slides having concave depressions, small crucibles which can be covered, or in capillary tubes with very thin walls. The last-named are particularly indicated if the reaction product is but slowly formed in a highly volatile liquid, since in a capillary tube evaporation is reduced to a minimum and the preparation may be allowed to stand for a relatively long time before being examined under the microscope.

**Method VI:** The reagent is incorporated into a natural or artificial fiber and the prepared fiber is dipped into the drop of solution to be tested. — The application of reagent-carrying fibers to microscopical analysis is due to Emich and Donau,<sup>4</sup> who first showed that certain reactions could be obtained by using carriers of reagents, which were impracticable in microscopical analysis by ordinary procedures.

<sup>4</sup> Emich: *Monats.* 22, 670 (1901); 23, 76 (1902); *Ann.* 351, 426 (1907).  
Donau: *Monats.* 25, 545 (1904); *Ann.* 351, 432 (1907).

One of the best examples is that of the valuable reagent  $\text{H}_2\text{S}$ . It was shown that a sulphide-carrying fiber laid in a drop could be made to indicate the presence or absence of the metals of the  $\text{H}_2\text{S}$  and  $(\text{NH}_4)_2\text{S}$  groups, the fibers being used first in acid, then in alkaline solution. So, too, most of our indicators of acidity and alkalinity when incorporated in silk or viscose-rayon afford sensitive and conveniently applied tests.

In developing a fiber method, certain properties must be borne in mind.

1. The fiber must possess a strong adsorptive property for the reagent.
2. The concentration of the adsorbed chemical must be relatively high in the prepared fiber.
3. The fiber should hold the chemical if possible, and not "bleed" too readily when it is immersed in the test drop.
4. The fiber must not react with the adsorbed reagent so as to change its chemical nature even on long standing.
5. The prepared fiber must afford as sensitive a reaction as the free reagent itself.

With the above properties governing the prepared fibers, the following have been found satisfactory. Silk impregnated with red and blue litmus; silk with Congo red; viscose-rayon with turmeric, potassium ferrocyanide, or potassium thiocyanate; wool or guncotton with zinc sulphide; silk or viscose-rayon with gold.

Two methods of using the impregnated fibers in testing have been proposed:

A. A slender conical cylinder of wax is affixed to the slide adjacent to the drop to be tested. To the point of the cone one end of the fiber is attached by gently pressing it against the wax. The upper part of the cone is bent over at about  $90^\circ$  with its vertical axis, and the free end of the fiber thus made to dip into the test drop. The liquid rises part way up the fiber by capillarity and when examined under the microscope the fiber is partly acted upon and partly free.<sup>5</sup>

B. A small shallow test drop is used and the fiber so placed that half of it lies immersed within the test drop and half outside the drop.<sup>6</sup> It is easy to follow the change in color, for both portions of the fiber can be seen in the same field of the microscope.

*Typical Applications:*

See Boron, Method A, page 170.

Zinc Sulphide Fibers, page 404.

<sup>5</sup> Emich: *loc. cit.*

<sup>6</sup> Chamot and Cole: *Jour. Ind. Eng. Chem.* 9, 969 (1917), 10, 48 (1918).

**Method VII:** A compound is added which will color the reaction product, usually by adsorption or solid solution, and thus increase the sensitivity of the test because of the formation of a color image. — Examples of the principles involved in Method VII are to be found in the use of stains and dyes for the differentiation of cellular structures of animal or of vegetable origin; in the staining of  $\text{Al}(\text{OH})_3$  with Congo red and  $\text{SiO}_2$  with malachite green; in the staining of fats with Sudan red or alkannin or of fatty acids with Nile blue; or the staining of starch with iodine.

Falling within the principle involved in Method VII is the coloring of alkali perchlorate crystals with permanganate and of those of silver sulphate with chromate.

No general directions are possible for tests performed under Method VII. Each individual test and reagent must be applied in accordance with the materials and the conditions involved.

*Typical Applications:*

See Manganese, Method A, page 261.

Perchlorates, Method A, page 386.

Chromium, Method A, page 244.

**Method VIII:** Testing for the evolution of a gas by means of gels. — Gases generated within a gel or viscous liquid are held for a considerable time dispersed in the semi-solid medium in tiny bubbles.

The method serves as a means of ascertaining whether a substance dissolves with effervescence and gives off a gas under the influence of certain chemical reactions.

In general the method is not adapted to the identification of the gas given off, although in the case of some gases the gel may carry soluble compounds which will react with the gas set free in a reaction.

Dissolve in freshly boiled distilled water sufficient gelatin to make a gel that just "sets" on cooling. For a large drop of solution on an object slide one or two square millimeters of commercial sheet gelatin will be sufficient. It is essential that the gel shall not possess too high a setting power, nor be so "thin" that considerable time and a low temperature are required for it to set.

The substance to be tested, if a solution, is evaporated to dryness in a thin film upon an object slide; if a solid, it is finely powdered and spread in a thin layer over a circular area about 5 mm. in diameter. Upon the dry material a drop of melted gel is dropped and caused to spread out in a thin layer extending a very little beyond the circumference of the film of substance. It may be necessary to warm the object slide to prevent too rapid setting. The preparation is then laid upon a cool surface until the gel has set.

The preparation is placed upon the stage of the microscope and focused. It is now ready for the application of the reagent that is to be used to test for the generation of a gas. A large drop of the reagent is

placed close to the drop of jelly and brought into contact with it. As the reagent slowly diffuses into the gel it attacks the dry material. If a gas is set free, tiny bubbles will appear throughout the gel as tiny black disks with a bright center. They are, of course, spherical in form, and behave as do air bubbles. (See *Vol. I*, page 362.)

If the gas is very soluble in water and is liberated too slowly, bubbles will not remain visible for any appreciable time, but even under these conditions close observation will usually reveal their presence just as they are formed.

Other transparent gel-forming material may be substituted for the gelatin, or substances with a high viscosity, even if they do not form gels, may be used to good advantage.

Having ascertained that a gas is given off, it can be tested and possibly identified by employing the apparatus and procedure described in Method IX.

*Typical Applications:*

See Carbonates, page 323.

**Method IX: Identification of a gas or vapor by exposing a compound to the action of the gas or vapor.** — The apparatus shown in Fig. 10, page 17, has been found convenient for the production of reactions between a gas or vapor and a reagent in solution.

The material from which the gas is to be evolved is placed in the crucible, covered with a thin layer of freshly ignited asbestos fibers, and the reagent that is to cause the liberation of the gas is added. Before this is done a small object slide is prepared with a *very small* drop of the absorbing (or "fixing") compound. Immediately on the addition of the liberating agent, the object slide is inverted over the crucible, with the hanging drop at the center of the crucible opening. Crucible and cover are placed in the clamp so as to close tightly the apparatus and prevent the escape of gas. The crucible is then *gently* warmed to favor the decomposition of the material being tested and the diffusion of the gas so as to bring it in contact with the hanging drop. After a short interval, and before any appreciable amount of steam has condensed, the slide is removed, turned over, and the drop of liquid examined under the microscope either directly or after the addition of a suitable reagent. If a reagent is contained in the hanging drop, the formation of a precipitate may often be observed under the microscope without uncovering the crucible, thus increasing the sensitivity of the test.

When dealing with very small amounts of a readily diffusible gas or vapor, and when there is believed to be danger of loss, it may be wise to cover the crucible with the prepared slide before the liberating reagent is

added, leaving a small opening through which the liberating reagent is added through a capillary pipette. The cover is slid over the opening the instant the reagent has been added.

This procedure is applicable to the detection of gases such as  $\text{CO}_2$ ,  $\text{HCN}$ ,  $\text{H}_2\text{S}$ , etc., and vapors of  $\text{Br}_2$ , etc. It is also of value in the oxidation of loosely bound sulphur by  $\text{Br}_2$  vapors and in the chlorination or oxidation of compounds by  $\text{Cl}_2$ .

**IXA:** If a fragment of a solid reagent is to be exposed to gas evolved in "micro" volume, the apparatus illustrated in Fig. 27 can be used. — The gas generated or liberated in the retort *G* passes over the reagent *S* in the capillary tube *T*, and the progress of the reaction can be followed under the microscope.

When employing this apparatus there should always be a loose wad of absorbent cotton, glass wool, or asbestos at *C*, to prevent the mechanical carrying over of particles from the effervescing material, or droplets of water or liberating reagent. The capillary tube *T* is attached to the retort by means of a short piece of rubber tube *R*. The tubulation is closed by a wooden or rubber plug *P*. The manipulation of the component parts of the apparatus will be obvious from the diagram. (See Arsenic, Method A, page 222.)

For the observation of the reagent *S* the tube is held upon the stage of the microscope by means of the stage clips, the fragment *S* being moved to the center of the field. It is always best to lay *T* upon an object slide, and after clamping in place, a large drop of immersion oil is applied at *S*. This eliminates the heavily contoured refraction image of the tube and enables the worker more readily to follow changes in the reagent fragment.

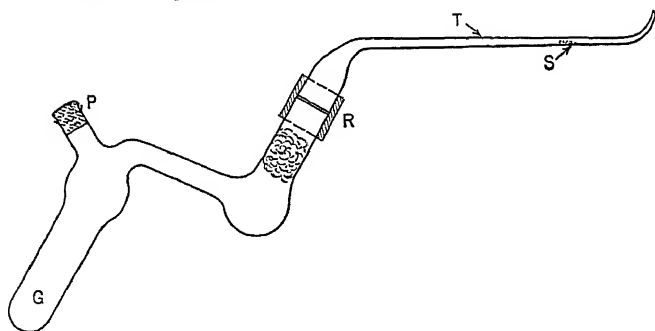


FIG. 27. Apparatus for the Detection of an Evolved Gas. (Actual size.)

When the gas evolved is heavier than air the drawn-out tip of the tube should be turned up as shown in the diagram, but if the gas is lighter than air the tip should be turned down.

When the tip is turned down a gas can be made to pass into a drop of reagent in which a reaction may be produced.

For further details see Detection of Arsenic, page 222.

*Typical Applications:*

See Ammonium, pages 74, 75.

Arsenic, Method A, page 222.

Bromides, Method 1, page 376.



**Method X: Testing with hydrofluoric acid, ammonium bifluoride, or with fluosilicic acid.**— Before undertaking any tests or performing reactions in which fluorine compounds are used as reagents in neutral or acid solutions, it is necessary to take steps to guard against injury to microscope and accessories by the corrosive action of any HF that may be set free. Unless these precautions are taken, there is great danger of permanently damaging the objectives, the condensers, and the polarizing prisms.

First, remove all objectives from the nosepiece save the one that is to be used; this will probably be the 32-mm. or the 16-mm. objective. Remove the substage condenser and the polarizer, and set all these accessories far to one side on the work table where they will be safe from attack by HF fumes.

Protect the objective by a shield such as is shown in Fig. 28. This consists of a brass cylinder fitting over the objective and made gas tight by a rubber ring. In the lower opening of the cell a No. 1 cover-glass is sealed in place with Canada balsam, shellac, or other resin. Before using the objective to view the preparation, examine the sealed-in window to make certain that the cement is free from holes or fissures.

If a protecting cell is not available, place a large drop of immersion oil upon the bottom lens of the objective and press a small No. 1 cover-glass against the lens. The cover-glass will remain in place and the lens will be protected from HF fumes for the short periods required for an examination of the preparation. Oil is safer than glycerin for attaching the protecting cover-glass to the objective.

As a further precaution *work quickly*. Do not allow a preparation to remain more than a few seconds at a time on the stage under an objective. Use as low a power (long working distance) as is consistent with a satisfactory resolution of the crystals formed in the test drop.

If a number of preparations are to be studied, it is wise to remove the cover-glass from time to time, wipe off the oil, and add a fresh drop of oil and a new cover-glass, for although HF is theoretically not soluble in oil it will be found that objectives are nevertheless attacked after long exposures and continued usage.

It is always good practice to relegate an old objective to work with HF, for if damaged the loss is negligible.

Reactions involving HF may not be performed on glass object slides,

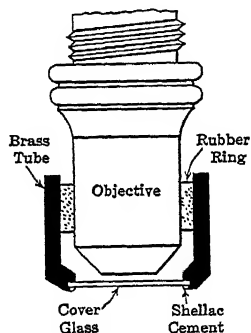


FIG. 28. Shield for the Protection of Objectives.

because they will be attacked and various fluosilicates will be formed. Platinum foil or lead foil cannot be used because they are opaque. Glass stirring rods cannot be employed. Use a platinum wire.

An object slide may be protected by coating it with Canada balsam and baking it in an oven until the varnish has lost practically all its

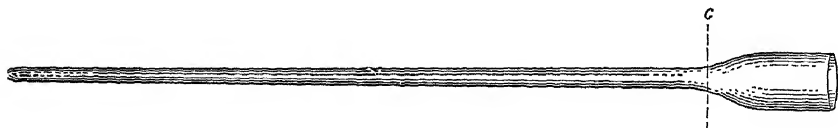


FIG. 29. Capillary Tube for Sublimations. (Full size.)

volatile components; when cool the slide should have a hard thin film, free from air bubbles and fissures. Always examine the surface under the microscope to be sure that no openings are present. Or the slide may be rendered safe by a coating of "Duco," "Bakelite," or other synthetic base varnish. These varnishes properly applied to *clean* object slides are not likely to fissure on drying or baking, an almost ever-present source of trouble when using the older types of varnish.

Far better than coated slides are slips  $35 \times 25$  mm. cut from 1-mm. thick sheets of celluloid. Since these materials are free from  $\text{SiO}_2$  and alkali salts, reactions involving the use of  $\text{HF}$  or  $\text{NH}_4\text{F} \cdot \text{HF}$  can be performed without fear of contamination by objectionable compounds.

The objection to cellulose nitrate and cellulose acetate object slides is that it is difficult to find pieces that are not badly scratched or full of other defects. Moreover, they are slowly attacked by  $\text{HF}$ . They are also quite easily softened by heat and the former are very flammable. If it is necessary to heat a preparation, it is unwise to use a free flame; it is safer to heat a metal plate to the requisite temperature and lay the preparation upon it. (See Fig. 1, page 5; Fig. 3, page 8.)

When it is necessary to heat, rather than warm a preparation, this should be done on platinum foil, and after cooling the material can be transferred to a transparent slide for examination under the microscope.

Method X can be used in the detection of the elements Si, Ti, Zr, Ge, Cb, Ta, Na, Ba, Li, Al.

*Typical Applications:*

See Sodium, Method C, page 62.

**Hydrogen-Ion Concentration.** — The determination of hydrogen-ion concentration, though properly belonging to the field of quantitative analysis, is frequently of use in microscopical work, even though only approximate values are obtained. Recognition of the presence of

"strong" or "weak" acids or bases, or of their salts, is sometimes useful as confirmatory evidence in identity tests. The addition of a buffer salt such as ammonium acetate is common practice when the presence of strong acids interferes with the tests in question. The control of the acidity or alkalinity of solutions in which reactions are to be carried out deserves more emphasis than it usually receives in analytical work.

Very exact determinations upon small drops are perfectly practicable by electrometric methods using microelectrodes which may be handled by a micromanipulator and thus introduced into organs, tissues, cells, tiny droplets, etc.<sup>7</sup>

**Colorimetric determinations** by means of indicators are more convenient and are usually sufficiently accurate for most work. In order that colors may be compared under the microscope, a relatively intense color tint is necessary unless reflected light is employed and the preparation is viewed upon a pure white field, or unless preparations and standards are contained in capillary tube cells and observations are made with a comparison microscope or a comparison eyepiece. (See *Vol. I*, pages 37, 67, 182.) Test drops spread out upon a slide usually give too thin a layer of liquid to permit color differentiations by transmitted light. Drops standing up in tiny spheres upon an oiled slide yield an image too heavily contoured to be practicable, although such spherical drops can be employed by using reflected light and a white background.<sup>8</sup>

Fibers impregnated with the dyes used as indicators do not yield results that are readily interpreted, though they may serve in rough estimates of "acidity" or "alkalinity"; e.g., litmus silk fibers as applied to solutions give a red or a blue as the case may be, but variations in hue due to slight changes in *pH* cannot be recognized on the colored fiber. Wholly aside from this, litmus may indicate, with certain substances, a neutrality at several quite different *pH* values.<sup>9</sup>

Since certain of the useful indicators are almost insoluble in water, the addition of a tiny fragment of the dye to the test drop is sometimes impracticable.

A solution of the dye in dilute alcohol is commonly used, and a tiny

<sup>7</sup> Lehmann: *Biochem. Zeit.* 139, 213 (1923).

Taylor: *Proc. Soc. Expt. Biol. Med.* 23, 147-50 (1925).

Taylor and Whitaker: *Protoplasma* 3, 1-6 (1927).

Keller: *Naturwiss.* 17, 100-3 (1929).

Deidar: *Zeit. wiss. Mikros.* 46, 361-8 (1929).

<sup>8</sup> Richards: *Science* 68, 185 (1928).

<sup>9</sup> Robinson: *Jour. Biol. Chem.* 53, 445 (1922).

droplet is added to the test drop.<sup>10</sup> If comparative estimates are to be made, solutions of known  $pH$  to which the same concentration of indicator has been added are used for the comparisons.

Comparison of test drop with standards can be made by microcolorimeters; by projecting into the field by means of the Abbe condenser a series of uniformly illuminated standards;<sup>11</sup> or by observing standards simultaneously with the field of view by means of a drawing camera. The image of one standard at a time is brought into the field in juxtaposition with the test drop. This is readily accomplished by tipping the mirror of the microscope or that of the camera or by moving the series of standards themselves.

To cover properly the range of  $pH$  values from 1 to 12, a series of overlapping indicators is necessary. A convenient series is as follows:

$pH$ Range		Indicator	Color Change	
0.2	1.8	Acid cresol red	red	to yellow
1.2	2.8	Meta cresol purple	red	yellow
2.6	4.2	La Motte yellow	red	yellow
3.0	4.6	Bromophenol blue	yellow	blue
3.8	5.6	Bromocresol green	yellow	blue
5.2	6.8	Chlorophenol red	yellow	red
6.0	7.6	Bromothymol blue	yellow	blue
7.2	8.8	Cresol red	yellow	red
8.0	9.6	Thymol blue	yellow	blue
8.3	10.	Phenolphthalein	colorless	red
9.2	10.5	Thymolphthalein	colorless	blue
10.2	12.0	Alizarin yellow R	yellow	lilac

For qualitative indications it is only necessary to find which of the above indicators give an acid color and which an alkaline color. Since the  $pH$  value for "neutrality" is 7, it is usually best to start with bromothymol blue (6.0 to 7.6). If the test drop gives a blue color with this indicator the  $pH$  of the drop is 7.6 or greater; if yellow, the  $pH$  must be about 6 or less, if green, the  $pH$  lies somewhere between 6 and 7.6, the numerical value depending upon whether a yellow green

<sup>10</sup> Indicators may be introduced into tissues or organs by pipettes handled by the micromanipulator. Schmidtman: *Zeit. wiss. Mikros.* 42, 81 (1925); Peterfi: *ibid.* 45, 56 (1928). The dye may be dissolved in collodion, which is evaporated to give a film, on which tiny droplets may be placed in a series and compared under the microscope. Wagner: *Biochem. Zeit.* 74, 239 (1916).

<sup>11</sup> Pantin: *Nature* 111, 81, (1923).

Needham: *Proc. Roy. Soc.* 98B, 259-86 (1925).

or a blue green hue is produced. According as the indication is blue or yellow, the next indicator overlapping higher or lower in the scale is chosen and the test made. This is continued until a point is found where one indicator gives an "acid" reaction and the next an "alkaline" reaction.

In this manner a fairly close estimate of the  $pH$  of the solution can be made without the necessity of employing standards and matching the color obtained with the final indicator used.<sup>12</sup>

Most qualitative tests are made upon solutions containing dissolved salts which exert a sufficient buffer action to enable reliable estimates to be made. In the absence of salts in solution a suitable buffer must be added. Space forbids a discussion of this phase of the problem.

Test papers, under the name "Hydriion" papers, for the estimation of  $pH$  from 1 to 14 are now available, together with suitable buffer solutions.<sup>13</sup> These papers, cut into tiny slips and dipped into test drops, afford a rapid and simple method of ascertaining roughly the  $pH$  of the aqueous solution in question. The strips may be examined with a hand lens or under the microscope by reflected white light and the color change compared with color charts furnished by the manufacturer with each of the five papers of different  $pH$  range.

Stated in terms of normality an acid solution having a  $pH$  of 1.0 is equivalent to a tenth normal solution; one having a  $pH$  of 2.0 is equivalent to a one-hundredth normal. An alkali solution having a  $pH$  of 13.0 is equivalent to a tenth normal alkali and one with a  $pH$  of 12.0 to a hundredth normal. That is to say that there is a change of one whole unit in  $pH$  for every change of  $10\times$  concentration above and below  $pH$  7.0, the "neutral" point.

For further information the reader is referred to texts devoted to the determination of hydrogen-ion concentration.<sup>14</sup>

<sup>12</sup> See Lundell and Hoffman: *Outlines of Methods of Chemical Analysis* (Wiley, New York, 1938), pp. 132-134, for a critical discussion of indicators and their applications. See also *The Determination of pH and Titrable Acidity in Pure Culture Study of Bacteria*, Vol. 6, No. 3, 1938 (published by the Commission on Biological Stains, Geneva, N. Y.), for an exceptionally comprehensive discussion of  $pH$ , its determination and sources of error.

<sup>13</sup> Sold by R. P. Cargille, 118 Liberty St., New York, N. Y.

<sup>14</sup> Clark, W. M.: *The Determination of Hydrogen Ions*. 3rd ed. (Williams & Wilkins Co., Baltimore, 1928).

Michaelis: *Hydrogen Ion Concentration* (Williams & Wilkins Co., Baltimore, 1926).

American Public Health Assoc.: *Standard Methods* (A. P. H. A., New York).

LaMotte Chemical Products Co.: *The ABC of Hydrogen Ion Control* (Baltimore).

Bausch & Lomb Optical Co.: *Hydrogen Ion Colorimetry* (Rochester, N. Y.).

**Determination of Molecular Weights.**—Barger<sup>15</sup> has devised an ingenious method for determining the molecular weight of substances in various solvents. It is based on the fact that the vapor tension of a solvent is lowered in proportion to the molar concentration of the dissolved material (dissociation being neglected), and that of two solutions the one having the higher molar concentration will have the lower vapor tension.

The substance of unknown molecular weight, in a solution of known concentration, is drawn into a 1.5-mm. capillary tube, alternately with a solution of a reference substance in the same solvent and having known molar concentration. A series of drops each about 1 mm. long, and separated by small bubbles of air, is thus formed in the capillary tube, and on standing for several hours at room temperature, or for a much less time at elevated temperature, isothermal transfer of the solvent takes place, from the drops of lower molar concentration to those of higher molar concentration. The length of the drops is measured before and after the run, by means of an eyepiece micrometer, and a comparison of the molar concentrations is made. By preparing several series, using reference solutions of different molar concentrations, the molecular weight of the unknown may be ascertained with considerable accuracy. For details of the method, especially as applied to organic substances, and for a full discussion of its accuracy and possible errors, the reader is referred to the original publications of Barger and Yamakami.

**Quantitative Estimation.**—Numerous reliable microanalytical methods for both inorganic and organic material have been developed by Donau, Pregl, Emich, and others.<sup>16</sup> The manipulative procedures are essentially those of macroscopical quantitative analysis, carried out on a greatly reduced scale. Since they do not involve the use of the microscope, except incidentally, they are not included in the present work. However, many of the methods of handling small amounts of material which have been developed in connection with microquantita-

<sup>15</sup> Barger: *Jour. Chem. Soc.* **85**, 286 (1904); **87**, 1756 (1905).

Yamakami: *Biochem. Jour.* **14**, 103 (1920).

Rast: *Berichte* **54**, 1979 (1921).

Emich: *Praktikum* (1931), p. 123; *Lehrbuch* (1926), p. 112.

Friedrich: *Mikrochemie* **6**, 97 (1928).

Jasinski: *Roczniki Chem.* **9**, 623 (1929).

<sup>16</sup> Donau: *Arbeitsmethoden der Mikrochemie* (1913).

Pregl-Roth-Daw: *Quantitative Organic Microanalysis* (1937); Pregl: *Die quantitative organische Mikroanalyse* (1930).

Emich: *Lehrbuch der Mikrochemie* (1926); *Methoden der Mikrochemie* (Abderhalden's *Handbuch der biologischen Arbeitsmethoden*, Lfg. 15); *Umsetzungen*

tive analysis will be found highly valuable in connection with microscopical qualitative examinations.

The rough estimation of the relative amounts of the various ingredients present in a mixture is sometimes possible in qualitative testing; it is based on the amount of precipitate obtained, and, if known mixtures or known dilutions are employed, can be of approximate quantitative significance.

It is also possible to measure with considerable accuracy the volume of a solution of known concentration required to effect complete precipitation in a micro test; the "end point" may be observed microscopically. This serves as a basis for volumetric analyses.

The solution can be measured dropwise by means of a small loop of fine platinum wire or a very fine pipette, previously calibrated. Graduated capillary pipettes, such as are used for dilution in blood counting, are very convenient. Ordinary drawn-out glass tubing, calibrated by weighing filled with mercury, and graduated in aliquot parts, can also be used.

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*kleiner Stoffmengen (Mikrochemie)* (Stähler's *Handbuch der Arbeitsmethoden in der anorganischen Chemie*. Bd. 2, Hfte. 2); *Mikrochem. Praktikum* (1931).

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Weygand: *Quantitative analytische Mikromethoden der organischen Chemie* (Akad. Verlag, Leipzig, 1931).

Pregl-Welter: *La micro-analyse organique quantitative* (Les Presses Universitaires de France, Paris, 1923).

Niederl and Niederl: *Micromethods of Quantitative Organic Elementary Analysis* (Wiley, New York, 1938).

## CHAPTER III

### THE DETECTION OF THE ELEMENTS OF GROUP I OF THE PERIODIC SYSTEM

Li; Na; K, (NH<sub>4</sub>), Rb, Cs; Cu, Ag, Au

Group I in the Periodic Classification of the elements consists of the transitional element lithium; a main subgroup — the alkali metals — sodium, potassium, rubidium, cesium; and a secondary subgroup — copper, silver, gold.

From the point of view of microscopical qualitative analysis lithium is strictly a transitional element more closely related to Group II, for although its very soluble halogen salts resemble those of the alkalis, its normal carbonate and its phosphates, being difficultly soluble in water, link it with the alkaline earths (calcium, strontium, and barium), but on the other hand, since its oxalate and sulphate are readily soluble, it is excluded from the analytical group calcium, strontium, barium. Moreover, lithium fails to yield crystalline precipitates with most of the reagents employed for the detection of the alkalis; hence analytically it falls in a group by itself.

Because sodium forms, with the halogens, crystals of the cubic system, similar to the like salts of potassium, rubidium, and cesium, sodium is to be regarded as a member of the alkali group, but, save for the halogen salts, most of the simple salts of sodium crystallize in systems different from those of potassium, rubidium, and cesium and differ from the salts of these elements in relative solubility and in analytical behavior. We may therefore consider that sodium like lithium falls in a separate analytical group.

To the potassium group of the alkalis, potassium, rubidium, and cesium, we must add the element thallium, since most thallic salts respond to the same reagents used for the detection of these elements. For the same reason we must consider the radical NH<sub>4</sub> as also a member of this group, since ammonium salts are very apt to be mistaken for potassium salts.

In the potassium group, when the metal is united to a simple anion the solubility of the salt usually rises with the atomic weight of the



element; but when in double or complex salts this relation seldom holds, and may on the contrary be quite the reverse, as for example, the chloroplatinates, chlorostannates, etc.

When the alkali metals are united with complex ions, very stable salts usually result; so stable, in fact, that it is sometimes difficult to obtain satisfactory tests for the component elements. In many instances it is necessary to heat the compound to be tested until the complex is destroyed, then treat with HCl or HNO<sub>3</sub>, or even aqua regia, and test the solution for the alkali metals.

The great majority of the double and triple salts with which the analyst comes in contact contain one or more alkali metals. The identification of these double, triple, or complex salts is most easily accomplished by observations of crystal habit and optical characters, after a chemical test has shown what cations and what anions are present.

The members of the secondary subgroup of Group I, copper, silver, gold, seldom enter into any scheme for the microscopical detection of members of the main or primary subgroup; hence the consideration of their analytical behaviors can be deferred until the discussion of the analytical groups into which each one properly falls. From their position in the periodic system, copper, silver, and gold are the links between Group I and Group VIII. It has therefore appeared to be more logical to treat these elements in connection with the discussion of the micro-analytical behavior of Group VIII; but in their lower valence, copper and gold (and thallium) are more closely affiliated with the other members of Group I than they are with the elements of Group VIII. These analogies are shown in the monovalent halogen compounds, in the isomorphism of CuCl and AgCl with NaCl, in the isomorphism of Ag<sub>2</sub>SO<sub>4</sub> with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and in the isomorphism of the "alums."

Although the halogen compounds of the elements of the secondary subgroup of Group I have formulas similar to those of the alkalis, they differ greatly from the alkalis in their properties. CuCl, AgCl, and AuCl are white salts, insoluble in water, but soluble in concentrated HCl, in NH<sub>4</sub>OH, and in alkali thiosulphates.

## DETECTION OF SODIUM

**A. By means of Uranyl Acetate** —  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2 \text{H}_2\text{O}$ .

*Compound Formed* —  $\text{Na}(\text{C}_2\text{H}_3\text{O}_2) \cdot \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$  or

$\text{Na}(\text{C}_2\text{H}_3\text{O}_2) \cdot \text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2 \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot x \text{H}_2\text{O}$ .

The reagent — a very concentrated solution of uranyl acetate acidified with acetic acid — is applied by Method III, page 35. The reagent drop should be large and highly concentrated.

The reaction product—sodium uranyl acetate—is a salt of high molecular weight, strong crystallizing power and low solubility in cold water. It is quite soluble in hot water and sufficiently stable (especially in the presence of free acetic acid) to permit recrystallization from hot water. This salt separates under the conditions of the test in the form of very faintly yellow regular tetrahedra or triangular plates of the cubic system. (Fig. 30, Fig. 32, page 53.) The crystals are therefore isotropic and can be easily differentiated from other uranyl salts which may separate, but which are anisotropic. The reagent separates in short, stout orthorhombic prisms.

Viewed under the microscope by transmitted light the perfect tetrahedra of this double acetate of sodium and uranyl sometimes appear to be black, on account of internal total reflection.

If instead of uranyl acetate, zinc uranyl acetate— $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ —is used as the reagent, in addition to the double acetate of sodium and uranyl there is formed a triple acetate of sodium, zinc, and uranyl which separates in very characteristic monoclinic polysynthetic twins possessing an octahedral aspect; these crystals appear to be colorless, but are in reality faintly yellow. (Fig. 33, page 53.) The advantage of employing zinc uranyl acetate instead of uranyl acetate is discussed on page 56.

No element other than sodium yields crystals in any way resembling the *double* acetate described above.

The reagent should be strongly acidified with acetic acid to prevent hydrolysis and to provide sufficient  $(\text{C}_2\text{H}_3\text{O}_2)^-$  ions to ensure the formation of the double and triple acetates which are to serve as the basis for the test.

Free mineral acids must be absent or not more than a trace be present. Ammonium acetate should not be used to mitigate the interference of free mineral acids since there is danger of the sodium reaction being inhibited or greatly retarded. Recourse should be had to evaporation or fuming off the excess of acid.

Ions uniting with uranium to form compounds insoluble in water or in dilute acetic acid may prevent the formation of the sodium double salt by removing the  $\text{UO}_2$  ions. Those most frequently met with are  $\text{CO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{OH}^-$ ,  $\text{PO}_4^-$ ,  $\text{Fe}(\text{CN})_6^-$ ,  $\text{P}_2\text{O}_7^-$ ,  $\text{AsO}_4^-$ ,  $\text{MoO}_4^-$ ,  $\text{WO}_4^-$ ,  $\text{SiF}_6^-$ . When any of these anions are present, uranium will be precipitated in the form of a granular or gelatinous compound usually appearing to be brown or black by transmitted light but often almost invisible unless care is used in the illumination of the preparation. In such an event the amount of uranyl acetate employed must be in excess of that required to unite with all of

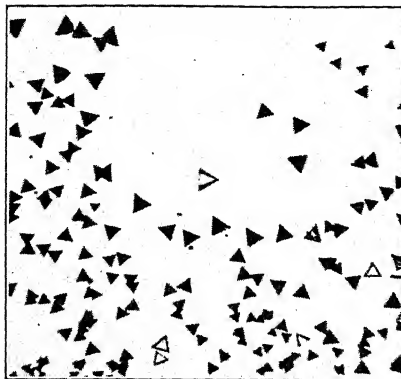


FIG. 30. Sodium with Uranyl Acetate. 60X.



FIG. 31. Potassium with Uranyl Acetate. 60X.

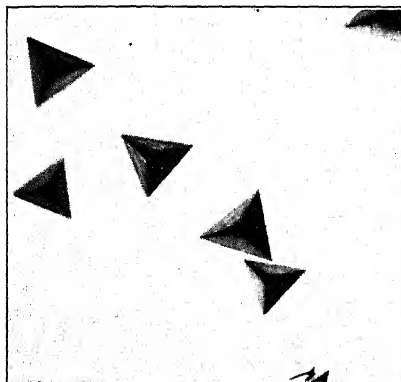


FIG. 32. Sodium with Uranyl Acetate. 300X.

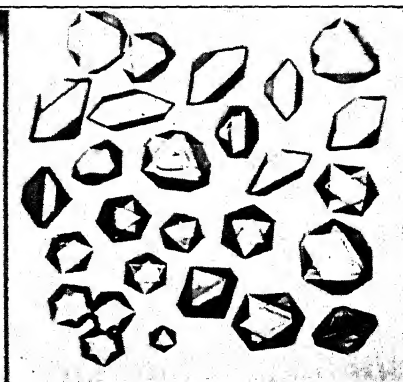


FIG. 33. Sodium with Zinc-Uranyl Acetate. 100X.

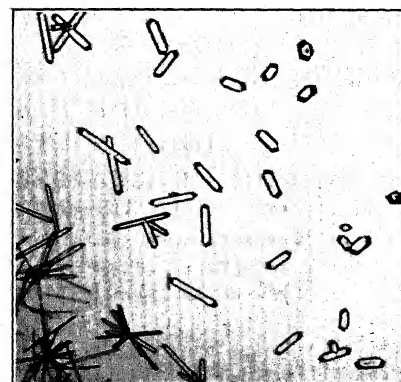


FIG. 34. Sodium with Bismuth Sulphate. 100X.

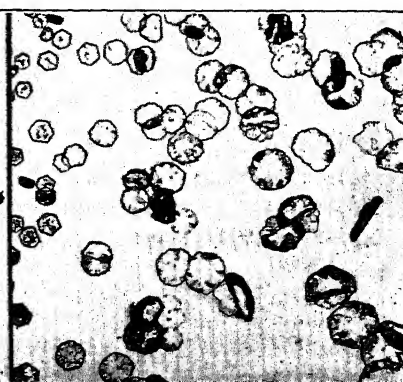


FIG. 35. Potassium with Bismuth Sulphate. 100X.

the precipitating ions present. To accomplish this completely, flood the dry film; after a few seconds decant or filter, transfer the clear solution to a clean slide, and allow to evaporate to crystallization; crush some of the crystals first formed so as to prevent the formation of a metastable solution.

When the solution of the reagent is being drawn across the dry film of the material to be tested, care should be taken to avoid flooding the entire film. If flooding does occur, it is usually best to prepare a new film and test anew.

Potassium, rubidium, cesium, thallium ( $\text{Tl}^+$ ), ammonium, and silver also form double uranyl acetates having the type formula  $M(\text{C}_2\text{H}_3\text{O}_2) \cdot \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ . But these salts separate in long slender needles or slender tetragonal prisms terminating in pyramids (Fig. 31, page 53; Fig. 120, page 183). These salts constitute an isomorphous series, as might be expected from the position of these elements in the periodic system; they are more soluble than the corresponding sodium salt and therefore do not separate so readily from solution. The ammonium salt is so soluble that it rarely separates until the preparation has evaporated substantially to dryness.<sup>1</sup>

Because sodium uranyl acetate differs in crystal habit and in solubility from the corresponding double acetates of the other alkali metals, it is possible to detect sodium and potassium ( $\text{Rb}$ ,  $\text{Cs}$ ,  $\text{Tl}^+$ ) simultaneously, providing potassium is not in too great excess. The sodium salt separates first, then as the test drop passes to dryness the potassium group salts appear. When the proportion of  $\text{Na}^+ : \text{K}^+$  reaches 1 : 3 the reaction for sodium is very poor and uncertain, and may completely fail when the ratio is 1 : 5 or greater.<sup>2</sup> These same ratios hold approximately for rubidium, cesium, and thallium. If, therefore, these elements are present in larger amounts than sodium, they must first be removed through the addition of perchloric acid or tartaric acid. The sodium salts of these two acids are so much more soluble that it is easy to decant the sodium-containing mother liquor from the precipitated perchlorates or tartrates. The decanted mother liquor is evaporated

<sup>1</sup> Lenz and Schoorl: *Zeit. anal. Chem.* 50, 263 (1911), suggested the use of  $(\text{NH}_4)\text{C}_2\text{H}_3\text{O}_2 \cdot \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$  as a reagent for sodium in place of  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ , because of the much greater solubility of the ammonium salt. Its crystal habit is also in its favor, but the sensitivity of the reaction for sodium is not increased and its use precludes the possibility of the simultaneous detection of other alkali metals when testing for sodium.

<sup>2</sup> Schoorl: *Zeit. anal. Chem.* 48, 604 (1909).

Lenz and Schoorl: *Zeit. anal. Chem.* 50, 263 (1911).

Behrens-Kley: *Mikrochemische Analyse*, p. 32.

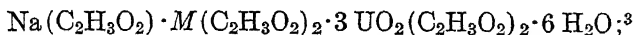
Chamot and Bedient: *Mikrochemie* 6, 13 (1928).

to dryness and tested as directed, or better still use zinc uranyl acetate as reagent.

*Acetates* of calcium, strontium, and lead, when tested as described, yield masses of colorless, fine, hair-like crystals (trichites) or exceedingly fine needles in clumps or bundles; occasionally long slender prisms may be formed. The bundles of needles appear brown by transmitted light. Barium acetate at first yields fine needles, but in a very short time large square plates appear which have a very characteristic appearance; finally, as the preparation goes to dryness, clusters and sheaves of relatively stout prisms are formed. The square plates appear to be constant and peculiar to barium. The composition of these interesting double(?) acetates of the alkaline earths is at present unknown.

When calcium, strontium, barium, lead, or lithium are present in larger amounts than sodium, the sensitivity of the sodium reaction is greatly reduced or the reaction for sodium may be completely inhibited. Boron may act toward sodium in a similar manner (Behrens). Sodium appears to be sometimes combined with these interfering elements in a complex which uranyl acetate is not powerful enough to destroy. Several evaporations to dryness with strong HCl will usually destroy the complex and permit the recognition of sodium. Sometimes a gentle ignition before the treatment with HCl will improve the character of the test; or even better, dilute H<sub>2</sub>SO<sub>4</sub> can be added, care being used to avoid any marked excess. The supernatant liquid is decanted from the precipitated sulphates, evaporated to dryness, and any excess of H<sub>2</sub>SO<sub>4</sub> is fumed off. The test for sodium is then made on the residue as usual. Lithium is, of course, not removed by this treatment, but can be precipitated as carbonate or phosphate, using the ammonium salts; but if either of these procedures is followed, it must be remembered that the residual carbonates must be destroyed with acetic acid and that PO<sub>4</sub><sup>---</sup> ions precipitate UO<sub>2</sub><sup>++</sup>.

When, in addition to sodium, certain bivalent cations are present, there will be formed, not isotropic tetrahedra, but weakly refractive anisotropic pseudo-rhomboheda, and bipyramids which are monoclinic polysynthetic twins (Fig. 33, page 53); members of an exceedingly interesting isomorphous series of salts having the general formula



<sup>3</sup> The water of crystallization of this salt is usually given as 6 H<sub>2</sub>O, but investigations have shown that it may be variable in amount, depending upon temperature and concentration. See Miholic: *Bul. Acad. Sci. Zagreb Univ.* 1920, 16. Chamot and Bedient: *Mikrochemie* 6, 13 (1928).

in which

$M$  may be  $\text{Cu}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Fe}^{++}$ .<sup>4</sup>

These triple acetates vary in their solubilities (some are deliquescent) and hence yield crystals varying in size in the test, but all have the same habit. As stated above, several of these triple acetates are known to exist as metastable compounds at temperatures above that of the room, hence the test should not be made upon a warm slide; all of them are prone to form metastable solutions, therefore before deciding that a test is negative, crush some of the material crystallizing at the edges of the reagent channel, and draw the fragments into the mother liquor.

All attempts thus far have failed to produce a difficultly soluble triple uranyl acetate of the type formula given above in which the  $\text{Na}^+$  is replaced by  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Tl}^+$ ,  $\text{Cu}^+$ ,  $\text{Ag}^+$ , or  $\text{Au}^+$ . However, under certain conditions  $\text{Ag}^+$ ,  $\text{Au}^+$ ,  $\text{Hg}^+$ ,  $\text{Hg}^{++}$ ,  $\text{Sb}^{+++}$ ,  $\text{Bi}^{+++}$ , when present, may interfere with the detection of sodium.

Since the sodium content called for by theory in these triple acetates is less than 2 per cent, one would expect that the sensitivity of this reaction for sodium would be considerably greater than that afforded by the double acetate. In practice, however, we find that there is little difference, the limiting value in each case being about 0.1  $\mu\text{g}$ . of sodium, when dealing with simple mixtures, while in the case of very complex mixtures or complex ions the sensitivity may fall to 0.5  $\mu\text{g}$ . The presence of the other alkali metals or of the alkaline earths does not inhibit the triple acetate reaction for sodium.

Taking advantage of this fact, we may use the zinc salt  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$  as a reagent for sodium, proceeding in the same manner as with  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2 \text{H}_2\text{O}$ . The zinc salt is employed rather than that of one of the other members of the isomorphous series since zinc can be obtained free from sodium. We have been unable to purchase samples of the acetates of other triple-acetate-forming bivalent elements, such as  $\text{Mg}$ ,  $\text{Cd}$ ,  $\text{Co}$ ,  $\text{Ni}$ , sufficiently free from sodium to permit their double uranyl acetates being used as reagents.

When the zinc double salt is employed as a reagent for the detection of sodium it is unnecessary first to remove the other alkalis or the alkaline earths unless these are present in very great excess.

Lithium forms triple acetates with uranyl acetate and the bivalent acetates listed above. In habit these lithium salts are identical in

<sup>4</sup> Caggioti: *Rend. accad. sci.* (3a) 33, 177 (1927), states that he has obtained  $\text{Na}(\text{C}_2\text{H}_3\text{O}_2) \cdot \text{Be}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 9 \text{H}_2\text{O}$  in rhombohedral uniaxial crystals, but neither Miholic nor Bedient was able to obtain a triple acetate with  $\text{Na}$  and  $\text{Be}$  when using spectroscopically pure  $\text{Be}$  unless the solution goes to dryness.

appearance with the corresponding triple acetates of sodium.<sup>5</sup> Hence when zinc uranyl acetate is used as a reagent for the detection of sodium, the formation of crystals having the appearance of those shown in Fig. 33, page 53, must not be interpreted as evidence of the presence of sodium unless lithium is proved to be absent.

The lithium triple acetate appears to be more soluble than that of sodium, requires a higher concentration for its separation, and forms more "obstinate" metastable solutions requiring seeding. Crystals of a triple acetate indicate sodium alone or lithium alone or both present.

According to Caley and Baker<sup>5</sup> lithium *does not* form a triple acetate with copper and uranyl. Were it not that copper uranyl acetate is not a satisfactory reagent for the detection of sodium in microscopical qualitative analysis, this reagent would be valuable for differentiating between  $\text{Na}^+$  and  $\text{Li}^+$ .

It is obvious that  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$  is a reagent of wider application than the mere detection of sodium. When applying this reagent the analyst may be guided by the following phenomena:

- A. Isotropic tetrahedra separate —  $\text{Na}^+$  present.
- B. Isotropic tetrahedra followed by tetragonal prisms —  $\text{Na}^+$ ; and  $\text{K}^+$ , or  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Ti}^+$ ,  $(\text{NH}_4)^+$ .
- C. Tetragonal prisms or needles only —  $\text{Na}^+$  may be present but other alkalis or alkaline earths interfere with  $\text{Na}^+$  test. Test with  $\text{ZnUO}_2$  acetate.
- D. Trichites or bundles or masses of very fine needles —  $\text{Ca}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Pb}^{++}$ ; ( $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Ti}^+$ ).<sup>6</sup>
- E. Monoclinic polysynthetic twins (pseudo-rhombohedral) —  $\text{Na}^+$  and (or)  $\text{Li}^+$  present *and* one or more of the following:  $\text{Cu}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Fe}^{++}$ .
- F. Square plates and masses of square plates —  $\text{Ba}^{++}$  ( $\text{Sr}^{++}$ ?).<sup>6</sup>
- G. Thin elongated plates with six sides and an acute angle of  $90^\circ = \text{AgC}_2\text{H}_3\text{O}_2$ ; acute angle  $49^\circ - 50^\circ = \text{AgC}_2\text{H}_3\text{O}_2 \cdot \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 = \text{Ag}^+$ . Both these compounds have parallel extinction.
- H. A heavy, more or less gelatinous, precipitate is produced. See page 52.

If the test drop is allowed to evaporate to dryness, spontaneously, there may appear *double* uranyl acetates of  $\text{Li}^+$ ,  $\text{Cu}^+$ ,  $\text{Cu}^{++}$ ,  $\text{Be}^{++}$ ; and if  $\text{Na}^+$  is absent,

<sup>5</sup> Felstein and Ward: *Analyst* 56, 245 (1931).

Adams, Benedetti-Pichler, and Bryant: *Mikrochemie* 26, 29 (1939).

Caley and Baker: *Ind. Eng. Chem. Anal. Ed.* 11, 604 (1939).

<sup>6</sup> These reactions are obtainable when the bivalent cations are combined with the acetate anion only, and no other anions are present in the drop to be tested.

orthorhombic double uranyl acetates of  $\text{Ba}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Pb}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Fe}^{++}$ . All of these double acetates are too soluble to be useful as identity tests and moreover they lack sufficiently characteristic habits.

When testing for the presence of mere traces of sodium, glass object slides should not be used; recourse should be had to object slides of quartz or fused silica or celluloid. Concentrations or evaporations to remove mineral acids must be performed on platinum foil or silica slides.

Because of its affinity for sodium, uranyl acetate or zinc uranyl acetate cannot be kept in glass vials where the salt will come in contact with the glass. Ebonite tubes or vials coated with ceresin wax or with a varnish may be used, or the reagent may be kept in paper rolls placed in a vial.

Always make a "blank" test on distilled water, acids, and all reagents, before deciding that traces of sodium are present in the material under examination.

Sodium-free uranyl acetate can seldom be purchased. Always extract the purchased uranyl acetate with 95 per cent alcohol, in which the sodium uranyl acetate is insoluble, using a platinum or silica container, crystallize the alcoholic extract in platinum or silica — use no glass.

#### Experiments. Test for sodium in:

- (a)  $\text{NaCl}$ ,  $\text{HNa}_2\text{PO}_4$ .
- (b)  $\text{NaKC}_4\text{H}_4\text{O}_6$ ; and in  $3(\text{Na}_2\text{C}_2\text{O}_4) \cdot \text{Fe}_2(\text{C}_2\text{O}_4)_3$ .
- (c) A mixture of  $\text{NaCl}$  and  $\text{MgCl}_2$ .
- (d) A mixture of  $\text{Na}_2\text{SO}_4$  and  $\text{ZnSO}_4$ .
- (e) A mixture of  $\text{NaCl}$  and  $\text{CoCl}_2$ .
- (f) Test for K in  $\text{KCl}$ .
- (g) Test for Tl in  $\text{TlNO}_3$ .
- (h) Test for Li in a Li salt.

#### B. By Means of Bismuth Sulphate — $\text{Bi}_2(\text{SO}_4)_3$ .

*Compound Formed* —  $3 \text{Na}_2\text{SO}_4 \cdot 2 \text{Bi}_2(\text{SO}_4)_3$ .

The best results appears to be obtained when the test is performed according to Method II, page 33.<sup>7</sup>

Prepare the bismuth sulphate as follows: Place two drops of concentrated  $\text{H}_2\text{SO}_4$  upon an object slide, add one drop of water, add  $\text{Bi}_2(\text{SO}_4)_3$  a little at a time with constant stirring and warming very gently until the solution appears to be almost saturated. Now add the least possible amount of dilute  $\text{HNO}_3$  required to make a clear solution.

Moisten with concentrated  $\text{H}_2\text{SO}_4$  a portion of the material to be tested, to convert to a sulphate. Heat so as to produce a stiff paste.

To the reagent drop add a small quantity of the pasty material to be tested. Warm gently. If sodium is present there should appear slender rods or short prisms with rounded or angular ends, singly or in crosses or X's, or in more or less star-like clusters (Fig. 34, page 53).

<sup>7</sup> Some analysts prefer to make the test by Method IIIA, carrying the evaporation of the test drop to complete dryness and applying a more dilute reagent than that described above.



The short, stout prisms are the most characteristic of the forms separating. Since characteristic crystals are formed only in warm solutions, it is essential to warm the preparation for a considerable time, for the crystals are usually slow in forming. Failure to detect sodium when this element is present in small amount often results from heating the preparation for too short a time.

The reagent drop must be perfectly clear and not so concentrated that, when warmed, sheaves and bundles of very fine needles appear. These needles are due to the separation of a bismuth sulphate of variable and uncertain composition. Not infrequently the acicular crystals develop into long, thin, colorless, lath-shaped crystals, singly, or in irregular crosses, sheaves, and radiating masses, but in a very short time the crystals disintegrate, dissolve, and are replaced by a second bismuth sulphate with a very different crystal habit, in the form of long, very slender, colorless needles, and hair-like crystals in large radiating clusters, sheaves, and fan-like masses. By transmitted light these aggregates of acicular crystals appear to be brown in color (structural color). It is probable that they are the result of the separation of an acid bismuth sulphate of unknown composition.<sup>8</sup>

Since the metastable bismuth sulphate which first separates forms crystals which may closely resemble the sodium-bismuth salt, it is a wise precaution, when in doubt, to divide the large reagent drop into two portions; to one of these add the material to be tested for sodium; the other portion is used as a "blank"; both are subjected to the same heat treatment and the drops compared under the microscope. If the reagent drop has been properly prepared and not too strongly heated, no crystals should appear.

The salt  $3 \text{Na}_2\text{SO}_4 \cdot 2 \text{Bi}_2(\text{SO}_4)_3$ , formed when sodium is present, may sometimes separate at room temperature, but this is unusual. Gentle heating of the preparation appears to be essential.<sup>9</sup> The characteristic crystals are small, stout, colorless prisms, rarely terminating in well-defined angles. They group themselves in a characteristic manner. Between crossed nicols they exhibit parallel extinction.

This reaction is peculiar to sodium and to bismuth; no other elements or compounds form similar crystals in strong  $\text{H}_2\text{SO}_4$ .

Potassium, rubidium, cesium, thallium, and ammonium form with the re-

<sup>8</sup> Mayrhofer: *Mikrochemie d. Arzneimittel und Gifte*, states that, on heating, a basic bismuth sulphate separates, but it is difficult to understand how such a salt can separate in the reagent as prepared above, *i.e.*, in the presence of an excess of  $\text{H}_2\text{SO}_4$  to which  $\text{HNO}_3$  has been added. Moreover the salt in question does not comport itself like any of the basic bismuth sulphates which have been described. See Heinz: *Pogg. Ann.* 63, 1844.

<sup>9</sup> See Behrens: *Anleit. mikrochem. Anal.* (1895), p. 34.

agent double sulphates having the general formula  $3 M_2SO_4 \cdot Bi_2(SO_4)_3$ . These five salts are isomorphous. They differ from the sodium double salt not only in habit but also in composition. The crystals first appear near the edges of the reagent drop or scattered through it, in the form of thin round disks (Fig. 35, page 53); disks with serrated circumferences; symmetrical rosettes (of the same appearance as in Fig. 38, page 61); skeletons of hexagons or as perfect hexagons (Fig. 36, page 61; Fig. 158, page 239). The rubidium and cesium salts seem to form thicker hexagons than do potassium and ammonium.

Since the potassium group double bismuth sulphates are more soluble than the sodium bismuth sulphate, the detection of both sodium and potassium in the same reagent drop is possible; the characteristic crystals of the sodium salt are the first to appear in the immediate neighborhood of where the fragment of the material being tested was introduced; later the potassium (or rubidium, cesium, ammonium) salt appears nearer the circumference of the drop. Even a very great excess of potassium does not interfere with the test for sodium. In dealing with such mixtures it is sometimes advantageous to retard the separation of crystals by introducing into the reagent drop a very minute quantity of glycerin.<sup>10</sup>

Having satisfied oneself as to the presence or absence of sodium after several repeated gentle heatings of the preparation and examinations, it is wise to heat the preparation sufficiently to cause a slight evaporation, and search the preparation for crystals of the potassium group double sulphates. Since we are no longer concerned with the sodium salt, the separation of needles or prisms of bismuth sulphate will cause no confusion.

Although free  $HNO_3$  may be present in the reagent,  $HCl$  is objectionable and may seriously interfere with the test.

Lithium forms a double sulphate with bismuth which may assume a habit closely resembling that of the potassium bismuth sulphate, but under the conditions of the test when performed as described there will be no precipitation of the lithium compound.

Salts of calcium, strontium, barium, lead, and silver,  $Tl^+$ ,  $Hg^+$ , which form difficultly soluble sulphates, may completely inhibit the test or may seriously affect its delicacy. The sulphates of all these elements are somewhat more soluble in concentrated  $H_2SO_4$  than in pure water, and from such solutions crystals may appear in forms somewhat resembling the sodium double sulphate. To guard against the possibility of error due to the presence of the above-mentioned elements it is best to remove them in part, before applying the test for sodium; this

<sup>10</sup> Behrens-Kley: *op. cit.*, p. 34 (1915).

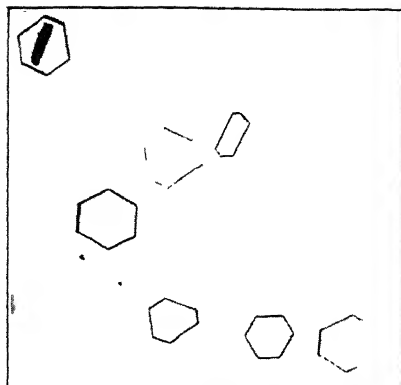


Fig. 36. Potassium with Bismuth Sulphate. 100X.

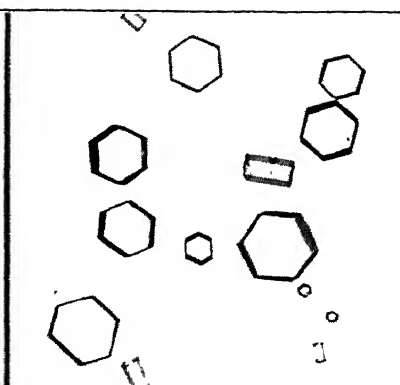


Fig. 37. Sodium with Ammonium Fluosilicate. 200X.

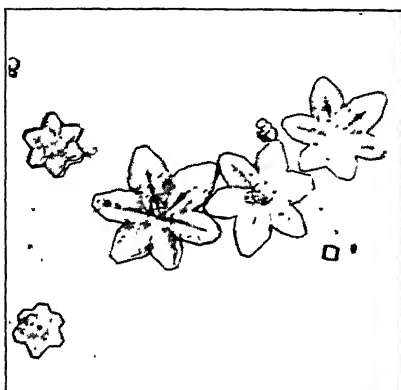


Fig. 38. Sodium with Ammonium Fluosilicate. 200X.

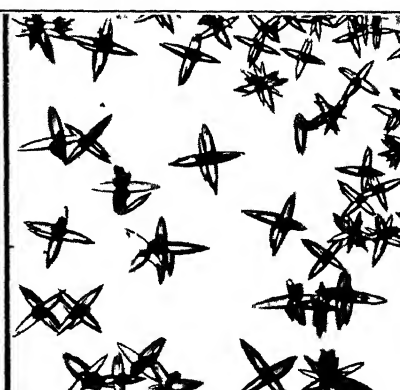


Fig. 39. Sodium with Potassium Antimonate. 100X.

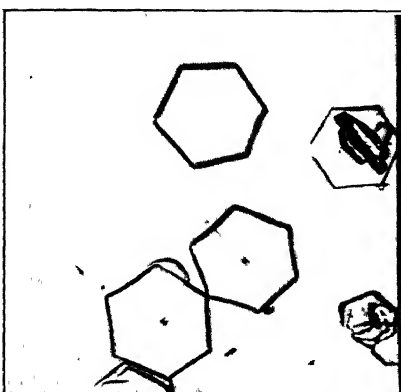


Fig. 40. Magnesium with Potassium Antimonate. 100X.

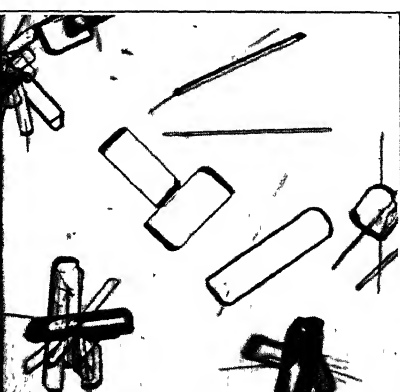


Fig. 41. Potassium with Tartaric Acid. 100X.

can be done by precipitating with dilute  $\text{H}_2\text{SO}_4$ . An excess of  $\text{H}_2\text{SO}_4$  must be avoided. The preparation is evaporated to dryness with gentle heat; the residue is extracted with a minimum quantity of water. The aqueous extract is evaporated to dryness and tested for sodium.

Much magnesium may also inhibit or greatly retard the separation of the sodium and potassium double salts. When both sodium and potassium are present with magnesium or lithium in great excess, lenticular and fusiform crystals are obtained, singly, in radiates or in irregular masses.<sup>11</sup>

Aluminum and other "alum"-forming cations may give rise to the formation of flattened octahedra having the appearance of hexagons only when a too dilute and not sufficiently acidic reagent is employed.

The bismuth sulphate test is more valuable for the detection of members of the potassium group than for sodium and is one of the best "micro" tests for bismuth since antimony gives no analogous reaction.

If no normal bismuth sulphate is available, the reagent can be prepared from basic bismuth nitrate (bismuth subnitrate) as follows. Place a tiny drop of concentrated  $\text{H}_2\text{SO}_4$  upon an object slide, add the basic bismuth nitrate a little at a time, with constant stirring, until no more dissolves; stir very thoroughly, for the solution of the basic salt is slow. Usually when saturation is reached and the basic salt is converted into a complex acid salt, the drop of acid suddenly becomes white, solid, and swells to a considerable degree. Add water *slowly and in very tiny amounts*, stirring after each addition. The white salt should dissolve almost completely, giving a clear colorless solution, or at the most, merely an opalescent one. Add one or two drops of  $\text{HNO}_3(1:4)$ . To the reagent thus prepared add the material to be tested.

**Experiments.** Test for sodium in:

- (a)  $\text{NaCl}$ .
- (b)  $\text{HNa}_2\text{PO}_4$ .
- (c) A mixture of salts of Na and K.
- (d) A mixture of salts of Na and Cs.
- (e) A mixture of salts of Na and Ca.

### C. By Means of Ammonium Fluosilicate — $(\text{NH}_4)_2\text{SiF}_6$ .

*Compound Formed* —  $\text{Na}_2\text{SiF}_6$ .

Apply the reagent by Method II (X), page 33, observing all the precautions given on page 43.

Before proceeding with the test always make certain that all the necessary precautions have been taken to guard against damage to the optical parts of the microscope.

<sup>11</sup> According to Kramer: *Mikroanalytische Nachweise anorganischer Ionen*, p. 23, these fusiform crystals are due to the formation of a quadruple salt potassium-sodium-magnesium-bismuth sulphate. Lithium under like conditions may form an analogous quadruple salt.

Use a celluloid, cellulose acetate, or varnished object slide. If the last, examine it under the microscope to be sure the varnish film is intact and free from holes or fissures.

Use a platinum or nickel wire for handling reagents, stirring, etc.

After adding the material to be tested to the reagent drop, warm the preparation by laying it upon a warm metal surface. Celluloid is very flammable and great care must be observed when the preparation is heated.

Sodium fluosilicate separates in rosettes (Fig. 38, page 61), in six-sided plates (Fig. 37, page 61), and in six-sided prisms with square or irregular ends or terminating in pyramids. These crystals are commonly ascribed to the hexagonal system but Winchell finds them to be biaxial with the refractive indices  $\gamma$  and  $\beta$  almost equal. The crystals are not hexagonal but orthorhombic (pseudo-hexagonal).<sup>12</sup>

Under the microscope by transmitted light the crystals of  $\text{Na}_2\text{SiF}_6$  appear to have a distinct pink color (Christiansen effect, see *Vol. I*, pages 190, 368). Since the indices of refraction of this salt are very close to that of water and the plates are thin, great care must be taken to illuminate the preparation properly; otherwise the presence of the crystals in the test drop may be overlooked. To guard against this source of error Kley<sup>13</sup> suggests allowing the preparation to evaporate to dryness at room temperature and covering the dry crystals with a liquid (benzene) having a higher index of refraction. (Monochlorobenzene,  $n = 1.52$ ; or monobromobenzene,  $n = 1.56$ , give somewhat better results.) Allowing the preparation to pass to dryness and examining the dry residue are also useful.

Lithium forms a fluoride  $\text{LiF}$  of lower solubility than the fluorides of the alkalis and may appear in the test drop as colorless, isotropic cubes and octahedra.

When members of the potassium group are present in a ratio of 20 parts to 1 of sodium, this test fails.<sup>14</sup>

In the presence of much calcium the hexagonal plates and short stout prisms are replaced by much longer and more slender prisms.

The fluosilicates of  $\text{Mg}^{++}$ ,  $\text{Fe}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Hg}^{++}$  corresponding to the formula  $\text{MSiF}_6 \cdot 6 \text{H}_2\text{O}$  form hexagonal (trigonal) prisms which are not to be confused with the rosettes and hexagons of the sodium salt; moreover they are much more soluble and do not appear until a high concentration has been reached. Never-

<sup>12</sup> Winchell: *Microscopic Characters of Artificial Inorganic Solid Substances or Artificial Minerals* (Wiley, New York, 1931), 2nd Ed. p. 180.

<sup>13</sup> Behrens-Kley: *Mikrochemische Analyse*, p. 34.

<sup>14</sup> Schoorl: *op. cit.*, p. 141.

theless it is wise to avoid applying the fluosilicate test until cations other than those of Group I have been removed.

Potassium, rubidium, and cesium form salts having the formula  $M_2\text{SiF}_6$ , which crystallize only from very concentrated solutions in the form of tiny, colorless cubes, octahedra, dodecahedra, and combinations of these forms. These salts are isomorphous and belong to the cubic system. There is no danger of mistaking a member of the potassium group for sodium; even when cubes in suspension are viewed with diagonals in line with the axis of the microscope and appear to have a hexagonal outline, careful illumination and focusing should dispel the illusion that these crystal are hexagonal plates. Hexagonal crystals may sometimes be formed.  $\text{K}_2\text{SiF}_6$  is usually isometric (hexagonal at  $10^\circ \text{C.}$  and below). When this salt separates in thin crystals it is even more difficult than the  $\text{Na}^+$  salt to detect because of its greater transparency; its index is 1.339 (Raiteri), but if  $\text{Al}^{+++}$  is present in the test drop the reaction product may have an index considerably higher. In minerals this value may reach 1.39 (Winchell).

The lithium salt  $\text{Li}_2\text{SiF}_6 \cdot 2 \text{H}_2\text{O}$  separates in monoclinic plates and prisms just as the preparation goes to dryness.

The salt  $\text{Ag}_2\text{SiF}_6 \cdot 4 \text{H}_2\text{O}$  is tetragonal but is too soluble to be useful as an indication of the presence of  $\text{Ag}^+$ .

Calcium, strontium, and barium unite with  $\text{SiF}_6^-$  to form an isomorphous series of monoclinic salts of the formula  $M\text{SiF}_6 \cdot 2 \text{H}_2\text{O}$ , crystallizing in curious fusiform bodies, singly, in crosses, radiating masses, and irregular bristling clumps. The calcium and strontium salts are far too soluble to separate, save when the preparation has evaporated completely to dryness, but the barium salt is sufficiently low in solubility to reveal the presence of barium as well as sodium in the same test drop.

Because of its high solubility  $\text{MgSiF}_6 \cdot 6 \text{H}_2\text{O}$  is not precipitated and only appears as the preparation goes to dryness, in the form of rhombohedra with strong birefringence.  $\text{Mn}^{++}$  and  $\text{Fe}^{++}$  are said to form salts isomorphous with the  $\text{Mg}^{++}$  salt. The crystal system of the zinc and cadmium salts has not been determined.

In the absence of  $(\text{NH}_4)_2\text{SiF}_6$ , a test for the presence of sodium (or barium) can be made by adding a little  $\text{SiO}_2$  to the test drop, following this by the addition of  $\text{NH}_4\text{F} \cdot \text{HF}$  or  $\text{HF}$ , and finally acidifying with  $\text{HCl}$  (or if barium is absent acidifying with  $\text{H}_2\text{SO}_4$ ). The preparation is gently warmed and set aside for a few minutes in order to give time for the crystallization of  $\text{Na}_2\text{SiF}_6$ .

These reactions are especially valuable in the analysis of silicates.<sup>15</sup> The finely powdered material is treated with  $\text{HF}$  or  $\text{NH}_4\text{F} \cdot \text{HF}$ , acidified, and the preparation treated as above described. But it must be borne in mind that other elements may appear in the place of silicon. If

<sup>15</sup> This system of silicate analysis was proposed 60 years ago by E. Bořický and described in a monograph entitled "*Elemente einer neuen chemischmikroskopischen Mineral- und Gestein-Analyse*" (Prag, 1877). It may justly be regarded as the first attempt at systematic microscopical qualitative analysis.

we write the general formula for this great group of fluosalts as  $M^{++}(RF_6)^{--}$  or  $M^{++}(RF_6)^{--} \cdot xH_2O$ ,  $M$  may be almost any element functioning as a cation and  $R$  may be silicon titanium, germanium, zirconium or tin. (See Fig. 113, page 151; Figs. 114, 115, 116, 117, page 173.) The alkali salts of these "fluo" acids do not form an isomorphous series.

Sodium fluogermanate,  $Na_2GeF_6$ , is isomorphous with  $Na_2SiF_6$ ; \* see page 173.

In the case of the acid  $H_2SnF_6$  a large number of salts have been made and described; some of these salts are polymorphic. Those which may separate upon the object slide in the course of a qualitative analysis are  $Li_2SnF_6 \cdot 2H_2O$ ;  $K_2SnF_6 \cdot H_2O(\alpha)$ ;  $CaSnF_6 \cdot 2H_2O$ ;  $SrSnF_6 \cdot 2H_2O$ ;  $BaSnF_6 \cdot 2H_2O$  and  $CuSnF_6 \cdot 4H_2O$ .

Fluosilicates of many organic compounds crystallize readily, and may separate in the course of a qualitative analysis.

### Experiments.

- (a) Test, as directed above, salts of Na in both neutral and acid solutions.
- (b) In order to appreciate better the reason for employing celluloid slips, place a drop of water on a glass slide, acidulate (but add no Na), then add the reagents and examine the preparation.
- (c) Try to obtain crystals of  $K_2SiF_6$  from KCl.
- (d) Add a little  $CaCl_2$  to a solution containing Na and test as above.
- (e) To a solution of NaCl add a little  $SiO_2$  or a trace of sodium silicate, then add  $NH_4F$  and an acid.
- (f) Repeat, using some Ti compound in place of that of Si. Then try in turn a compound of B; a compound of Zr; a compound of Ge.
- (g) Test a salt of Ba as above, then a mixture of Ba and Na. Note that it constitutes an excellent test for Ba even in the presence of Na.
- (h) Add to a solution of  $Al_2(SO_4)_3$  a large fragment of  $NH_4F \cdot HF$ .
- (i) Test a Li salt with  $NH_4F \cdot HF$ .

## DETECTION OF POTASSIUM

### A. By Means of Chloroplatinic Acid — $H_2PtCl_6$ .

*Compound Formed* —  $K_2PtCl_6$ .

Apply the reagent by Method I, page 31.

When a concentrated solution of  $H_2PtCl_6$  is caused to flow into a dilute solution of a salt of potassium, acidified with HCl, there separate at once well-formed, brilliant, highly refractive ( $n = 1.827$ ),<sup>16</sup> deep-yellow octahedra (Fig. 43, page 69), and combinations of octahedron and cube. Elongated and distorted shapes are also formed, and in shallow drops the octahedra, not being able to grow up or down, grow

<sup>16</sup> Raiteri: *Atti Accad. Lincei*, V, 21, I, 112 (1922).

laterally and assume the form of "flattened" octahedra whose relation to an octahedron is puzzling to the beginner. The elongated octahedra resemble orthorhombic crystals, but an examination between crossed nicols will show that they belong to the cubic system.

Not infrequently preparations are obtained in which twinning is very marked. Threelings and fourlings are also formed. In the case of twins, one type predominates; it results from the union in reversed position of the two halves of an octahedron where the dividing plane is parallel to the diagonally opposite faces of the octahedron.

The best-formed crystals and most satisfactory tests are to be obtained when the potassium ion is present in a chloride and the test drop contains a little free HCl, but much free HCl is to be avoided.  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$  does not inhibit the reaction but reduces its sensitivity; hence the analyst may be led astray in his estimate of the relative amount of potassium present. It is always best to remove free mineral acids by evaporating to dryness and "fuming off."

Since the salt  $\text{K}_2\text{PtCl}_6$  is only very slightly soluble in water (insoluble in alcohol), it is essential the the solution to be tested be quite dilute with respect to  $\text{K}^+$  ions; otherwise skeleton crystals, crystallites, and dendritic masses will be obtained instead of well-formed octahedra.

$\text{NH}_4^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Tl}^+$  form with  $\text{H}_2\text{PtCl}_6$  salts having the same composition and habit as the potassium salt and isomorphous with it. The solubilities of these salts decrease in the order named, and under normal conditions the size of the crystals separating in a test drop decreases with the rise of the atomic weight of the element (Figs. 43, 44, 45, page 69).  $\text{Cs}_2\text{PtCl}_6$  and  $\text{Tl}_2\text{PtCl}_6$  are so insoluble that it is almost impossible to obtain a dilution which will allow the formation of octahedra that can be resolved without a magnification of about 200. Usually skeleton crystals only are obtained in the form of six-pointed stars.

Because of the relatively great difference between the solubility of  $\text{K}_2\text{PtCl}_6$  and that of  $\text{Rb}_2\text{PtCl}_6$  and  $\text{Cs}_2\text{PtCl}_6$  it has been suggested that it is possible to differentiate between  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  by using a solution of  $\text{K}_2\text{PtCl}_6$  as reagent. Theoretically it should be possible so to adjust the concentrations that a solution of  $\text{K}_2\text{PtCl}_6$  will not give a precipitate with potassium salts but will at once precipitate rubidium, cesium, and thallium. In practice, however, this procedure is useless in dealing with material of wholly unknown composition.

The sodium salt  $\text{Na}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$  is so soluble that it rarely separates until the test drop has evaporated almost to complete dryness; it then appears as deliquescent, yellow, triclinic, tabular prisms, or as thin plates exhibiting brilliant polarization colors. These prisms are so



orientated upon the object slide that the observed extinction angle is about  $22^\circ$ .

The crystals of  $\text{Na}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$  are seldom well-formed, separate individuals, but occur in groups and aggregates at the periphery of the test drop; only the ends of the crystals projecting from the crystalline crust into the drop of liquid are well developed. Crushing the first crystals formed and drawing across the metastable solution will sometimes yield well-formed, separate prisms. This salt is so soluble that the addition of even strong alcohol will not induce crystallization.

$\text{Li}_2\text{PtCl}_6 \cdot x \text{H}_2\text{O}$  is even more soluble than the sodium salt, and consequently will not appear in routine analyses.<sup>17</sup>

$\text{BePtCl}_6 \cdot 8 \text{H}_2\text{O}$ , though very soluble, may usually be induced to crystallize as the test drop goes to dryness. The crystals are characteristic, thin, well-formed, square or rectangular plates, rectangular prisms, or "octahedra" belonging to the tetragonal system (Fig. 53, page 77); although faintly yellow in color they appear to be colorless by transmitted light under the microscope.

$\text{K}_2\text{PtCl}_6$  and  $(\text{NH}_4)_2\text{PtCl}_6$  differ so little in their solubilities that these two salts separate in crystals of the same size, appearance, and color. Under the conditions which obtain in the tests, it is not possible to differentiate between them. Hence before it is decided that potassium is present, ammonium must be proved to be absent. (See pages 73, 74.)

If  $\text{NH}_4^+$  ( $\text{NH}_3$ ) has been found, a little of the substance being analyzed is placed on platinum foil or in a tiny platinum cup and heated very carefully to dull red, no more, until all  $\text{NH}_3$  has been expelled. Test for potassium in the residue. Or add  $\text{NaOH}$  and boil to expel the  $\text{NH}_3$ . If  $\text{NaOH}$  is used, make a "blank" to assure the absence of potassium.

When much sodium, lithium, beryllium, or magnesium is present, it is important that the reagent drop be large and concentrated and that the analyst assure himself that sufficient  $\text{H}_2\text{PtCl}_6$  has been caused to flow into the test drop to provide sufficient  $(\text{PtCl}_6)^-$  ions to satisfy all the cations present which can unite with  $(\text{PtCl}_6)^-$  to form crystallizable salts under the conditions of the test.

Iodides and cyanides should be absent; otherwise very complex compounds may be formed which may seriously interfere with the detection of  $\text{K}$ ,  $\text{Rb}$ ,  $\text{Cs}$ , and  $\text{NH}_4$ .

<sup>17</sup> During the winter months the air is so dry in most of our American steam-heated laboratories that the chloroplatinates of sodium and beryllium, and sometimes even lithium, will separate. See also Gravestien: *Mikrochemie, Emich-Festschrift*, 135 (1930).

Chloro-acids analogous to  $\text{H}_2\text{PtCl}_6$  are formed by Ir, Ru, Rh, Pd, Os, and Sn. Similarly bromo-acids exist in which  $\text{Br}_6$  replaces  $\text{Cl}_6$ .

Many organic compounds, such as amino compounds, substituted ammonias, alkaloids, etc., unite with  $\text{H}_2\text{PtCl}_6$  to form crystalline compounds of relatively low solubility. Some of these give octahedral crystals of ammonium chloroplatinate or, as in the case of many alkaloids, crystals characteristic of the alkaloid will be obtained.

#### Experiments.

- (a) Test  $\text{KCl}$ ,  $\text{NaCl}$ ,  $\text{NH}_4\text{Cl}$  with  $\text{H}_2\text{PtCl}_6$ .
- (b) Test a phosphate, a sulphate, and a tartrate of potassium.
- (c) Test  $\text{K}_2\text{SO}_4$  in the presence of much  $\text{H}_2\text{SO}_4$ .
- (d) Test  $\text{RbCl}$ ,  $\text{CsCl}$ ,  $\text{TlNO}_3$ .

#### B. By Means of Perchloric Acid — $\text{HClO}_4$ .

*Compound Formed* —  $\text{KClO}_4$ .

Apply the reagent by Method I, page 31.

When a drop of moderately concentrated  $\text{HClO}_4$  flows into a drop of a cold, dilute, aqueous solution of a potassium salt there separate in a few seconds colorless orthorhombic prisms terminating in pyramids. The crystals separating from cold (*i.e.*, room temperature) solutions are better for identification purposes than those obtained in warm solutions.

In solutions concentrated with respect to  $\text{K}^+$  ions dendritic masses and skeletal crystals are formed which bear no resemblance to the prismatic crystals of  $\text{KClO}_4$ . Because of the low solubility of this salt these dendritic and skeletal forms almost invariably appear at first, and it is only after standing a minute or so that the well-formed crystals of characteristic habit are obtained.

The crystal forms which serve best to identify potassium are short, stout prisms, resting on a prism face or rarely on a pyramid face, and thin plate-like rhombs which later develop into prisms (Fig. 42, page 69). There are also always formed rectangular plates and prisms; but, since many other salts yield rectangular prisms, it is best to ignore them and depend upon the other types for the identification of potassium.

The crystals of  $\text{KClO}_4$  are orthorhombic, weakly birefringent, and are only moderately refractive ( $\beta = 1.47+$ ).

Rubidium, cesium, thallium ( $\text{Tl}^+$ ), and ammonium form crystals having the same habit as the potassium salt and isomorphous with it.

Unlike the chloroplatinates and chlorostannates the solubilities of these salts do not decrease with the rise in atomic weight.

If the solubility of  $\text{KClO}_4$  is taken as 1, the relative solubilities of

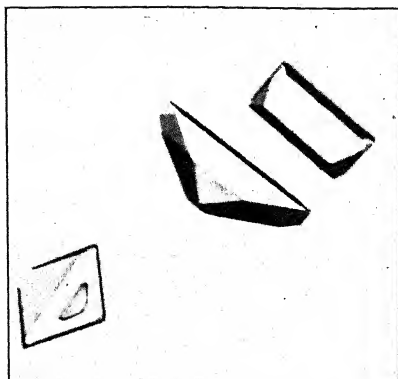


FIG. 42. Potassium with Perchloric Acid. 100 $\times$ .

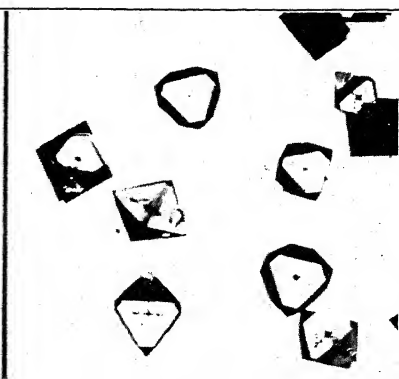


FIG. 43. Potassium with Chloroplatinic Acid. 100 $\times$ .

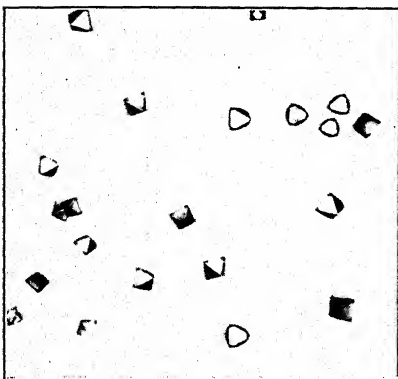


FIG. 44. Rubidium with Chloroplatinic Acid. 200 $\times$ .



FIG. 45. Cesium with Chlorostannic Acid. 200 $\times$ .

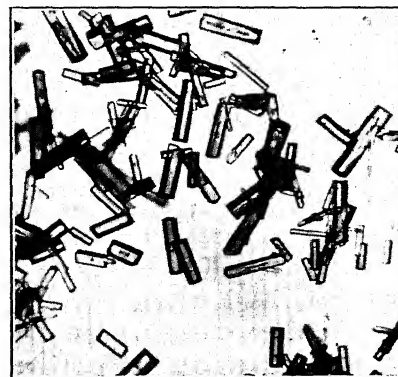


FIG. 46. Rubidium with Silver Chloride and Chloroauric Acid. 300 $\times$ .



FIG. 47. Cesium with Silver Chloride and Chloroauric Acid. 300 $\times$ .

the perchlorates of the alkalis can be expressed thus— $K^+ : Rb^+ : Cs^+ : Tl^+ : NH_4^+ : Na^+ = 1 : 0.72 : 0.96 : 9.6 : 13.4 : 57.7$ . These figures are only approximate. At room temperature, the solubility curves of the perchlorates of  $K^+$ ,  $Rb^+$ ,  $Cs^+$  are substantially parallel, but rapidly diverge at higher temperatures.

The sodium salt  $NaClO_4 \cdot H_2O$  is probably more soluble than the above ratio shows, and its solubility varies greatly with the concentrations of other salts which may be present.<sup>18</sup>

The salt  $NaClO_4 \cdot H_2O$  separates below  $52^\circ C.$ , but at temperatures above  $52^\circ C.$ , the anhydrous salt  $NaClO_4$  is obtained. Here again we find sodium at variance with the member of the potassium group.

$LiClO_4 \cdot 3 H_2O$  is hexagonal and very deliquescent.

The perchlorates of other cations which are commonly associated with the potassium group are all too soluble in dilute aqueous solutions to interfere with the detection of potassium.

$KMnO_4$  is isomorphous with  $KClO_4$ . This is of considerable theoretical interest since manganese and chlorine are both members of Group VII, and should show a somewhat close relationship. Practical advantage is taken of this isomorphism to increase the delicacy of the reaction for  $K^+$  ions and also the reaction for  $ClO_4^-$ . In the case of  $K^+$  ions, sufficient  $NaMnO_4$  is added to give the drop a deep pink color. Or in the absence of  $NaMnO_4$ , "sodium manganate," a salt of very uncertain composition, can be employed, since in acid solution it changes over into permanganate with the precipitation of  $MnO_2$ . Under these conditions, any crystals of  $KClO_4$  which are formed take up  $KMnO_4$  and become colored pink or dark rose. Since colored crystals are more easily detected in white light than colorless crystals, the sensitivity of the reaction is apparently increased. In this case, however, the sensitivity of the reaction is actually increased, for it has been shown that the solubility of  $KClO_4$  is lowered in the presence of  $KMnO_4$ .

Permanganate ions, likewise, are taken up by crystals of  $Rb^+$ ,  $Cs^+$ ,  $NH_4^+$ , and  $Tl^+$  perchlorates.

If a precipitate is obtained with  $HClO_4$ ,  $NH_4^+$ ,  $Rb^+$ ,  $Cs^+$ ,  $Tl^+$  must be proved to be absent before the conclusion may be reached that  $K^+$  is present. Recourse can be had to chemical tests or to optical constants to differentiate between this group. Since the test drop is usually acidified with  $HCl$ ,  $Tl^+$  ions need not concern us because of the low solubility of  $TlCl$  and its detection before  $HClO_4$  is added.

When care is taken to test only dilute solutions the potassium group alone will be precipitated; all other perchlorates are too soluble to appear under the conditions which obtain in a properly performed test.

<sup>18</sup> Cornec and Dickety: *Bul. Soc. Chim.* 1927. 1017.

Although  $\text{KClO}_4$  is insoluble in alcohol, the sensitivity of the test does not appear to be increased by exposing the test to alcohol vapors, nor is the separation of the crystals materially hastened.

The most satisfactory reagent is 70 to 72 per cent vacuum-distilled pure  $\text{HClO}_4$ . Blank tests should be made to ascertain whether the acid has become contaminated by potassium from the glass container.  $\text{NH}_4\text{ClO}_4$  may be used as a substitute for  $\text{HClO}_4$ .

Many organic compounds, as for example alkaloids, yield with  $\text{HClO}_4$  compounds of low solubility which may separate in well-formed crystals in concentrated test drops.

#### Experiments.

(a) Try the  $\text{HClO}_4$  reaction with different salts of K.

(b) Introduce  $\text{NaMnO}_4$  into the test drop, and test as above.

(c) Make a mixture of K and Na salts. Treat a drop of a solution of this material with  $\text{HClO}_4$ , evaporate, treat with the reagent again, and again evaporate, extract the dry residue with alcohol, and test the alcoholic extract for sodium with  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ .

(d) Try the action of  $\text{HClO}_4$  on members of the magnesium group, and upon members of the calcium group.

#### C. By Means of Bismuth Sulphate — $\text{Bi}_2(\text{SO}_4)_3$ .

*Compound Formed* —  $3 \text{K}_2\text{SO}_4 \cdot \text{Bi}_2(\text{SO}_4)_3$ .<sup>19</sup>

See Sodium, Method B, page 58.

When rough disks appear the conclusion is not always justified that some member of the potassium group is present. A decision should not be reached until sufficient time has elapsed to permit the formation of well-defined hexagonal plates. On long standing, thick six-sided tabular crystals may separate which may be mistaken for  $3 \text{K}_2\text{SO}_4 \cdot \text{Bi}_2(\text{SO}_4)_3$  unless examined between crossed nicols; but if this is done they will be seen to be polysynthetic and strongly birefringent, showing brilliant polarization colors. The hexagons of potassium bismuth sulphate are not polysynthetic and are weakly birefringent.

It will be noted that the reaction product is believed to have the composition  $3 \text{K}_2\text{SO}_4 \cdot \text{Bi}_2(\text{SO}_4)_3$ .<sup>20</sup> It is important to bear in mind this ratio of *three* molecules of potassium sulphate to *one* of bismuth sulphate, because it is often necessary to make several trials with different proportions of substance and reagent before a truly satisfactory crystallization can be obtained.

Too high a concentration of reagent and test substance gives rise to too rapid crystal formation and the separation of disks only.

<sup>19</sup> According to some investigators this double salt sometimes crystallizes with  $2 \text{H}_2\text{O}$ .

<sup>20</sup> Caglioti and Stoffi: *Atti Real Accad. Lin.* 5, 896 (1927).

Disks and plates on edge (Fig. 35, page 53; Fig. 36, page 61; Fig. 158, page 239) appear to be rectangular prisms with more or less rounded or beveled ends. These must not be confused with the characteristic prisms of the sodium salt (Fig. 34, page 53).

Rubidium, cesium, and ammonium form double bismuth sulphates having the same habit as the potassium salt. The cesium salt may often, however, be readily recognized, because the hexagons are thicker and have their edges beveled with pyramid faces; these faces are very rare when potassium only is present.

**D. By Means of Sodium Tartrate and Tartaric Acid —**  
 $\text{HNaC}_4\text{H}_4\text{O}_6 \cdot 4 \text{H}_2\text{O} + \text{H}_2(\text{C}_4\text{H}_4\text{O}_6).$

*Compound Formed —*  $\text{HKC}_4\text{H}_4\text{O}_6.$

Perform the test by Method III, page 35.

It is essential that the material to be tested be neutral, or at the most, only very slightly acid. If strongly acid, add sodium acetate.

The dry film across which the reagent is to be drawn should be thicker than is usual in making tests by this method. This is done by evaporating to dryness one drop after another on the same spot.

The reagent consists of a rather concentrated solution of tartaric acid to which a small amount of sodium tartrate has been added. An excess of tartaric acid is used in order to assure the formation of the acid salt  $\text{HKC}_4\text{H}_4\text{O}_6$ , instead of the normal salt  $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ , since the former is less soluble and its crystal form is more characteristic of potassium.

$\text{HKC}_4\text{H}_4\text{O}_6$  separates in short, stout, irregular orthorhombic prisms which are strongly birefringent but only moderately refractive. Hemihedral and skeletal forms predominate. Thin almost rectangular plates and tablets are also formed, which when viewed edge-wise appear to be slender prisms (Fig. 41, page 61).

Better and more reliable results are obtained when sodium tartrate is used in the reagent than when the test is made with tartaric acid alone. But if too much sodium salt is added there is danger of the formation of the double salt  $\text{NaK}(\text{C}_4\text{H}_4\text{O}_6) \cdot 4 \text{H}_2\text{O}$ ; this salt is not only less characteristic, but is more soluble than  $\text{K}_2(\text{C}_4\text{H}_4\text{O}_6)$  and is over 200 times as soluble as  $\text{HK}(\text{C}_4\text{H}_4\text{O}_6).$

The  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{NH}_4^+$ , and  $\text{Tl}^+$  acid tartrates of the formula  $\text{HM}(\text{C}_4\text{H}_4\text{O}_6)$  are isomorphous with the salt  $\text{HK}(\text{C}_4\text{H}_4\text{O}_6).$  The rubidium and cesium acid salts are even less soluble than the potassium salt.

$\text{Rb}_2\text{C}_4\text{H}_4\text{O}_6$  and  $\text{Cs}_2\text{C}_4\text{H}_4\text{O}_6$  are hexagonal (trigonal).  $(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$  is monoclinic. These salts can be differentiated by their optical properties.

Although  $\text{H}(\text{NH}_4)\text{C}_4\text{H}_4\text{O}_6$  is isomorphous with  $\text{HKC}_4\text{H}_4\text{O}_6$ , the former salt usually separates, under the conditions of the test, in forms such that a close observer can distinguish between the two salts providing  $\text{NH}_4^+$  and  $\text{K}^+$  are not both present in the test drop under examination. These two acid tartrates can be differentiated by an observation of their optic axial angles, that of the ammonium salt being approximately half that of the potassium salt.

Many other elements form tartrates of low solubility, yielding crystals which may separate under the conditions that obtain in the test. These crystals, although of not the same habit as the potassium salt, may bear a sufficiently close resemblance to it to lead to error unless checked on known material or by other methods. (See Fig. 72, page 109.)

Always study the preparations before they go to dryness, since double tartrates are almost invariably formed. There are so many possible combinations that it is almost impossible to become familiar with the crystal habits of all these salts, and as a result, their formation as the drop just goes to dryness is always puzzling to the analyst.

Sodium tartrate may be employed for the identification of calcium and to differentiate between strontium, barium, and lead. (See page 120.)

In some cases it is advantageous to mix, in a centrifuge tube, the reagent, the solution to be tested, and an equal volume of 95 per cent alcohol. The mixture is allowed to stand for a short time and centrifuged. The crystalline precipitate collecting at the bottom of the tube is transferred to an object slide and examined under the microscope.

## DETECTION OF AMMONIUM

**Treatment of the Substance Prior to Making the Identification Test.**—The radical ammonium functioning as the cation  $\text{NH}_4^+$  so closely resembles the cations  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  in its behavior toward the reagents employed for the microscopical detection of the elements of Group I that no test can be regarded as truly specific unless applied to the  $\text{NH}_4^+$  (*i.e.*,  $\text{NH}_3$ ) set free from its salts and absorbed in a suitable manner.

The expulsion of  $\text{NH}_3$  and subsequent fixation may be accomplished in a satisfactory manner by Method IX, page 41, employing the apparatus shown in Fig. 10, page 17.

The material to be tested is placed in the crucible, a drop of distilled water added, and sufficient freshly ignited asbestos dropped in just to cover the solution. A drop of  $\text{NaOH}$  solution is added and the crucible immediately covered with an object slide carrying a hanging drop of

dilute HCl. Gentle warming will expel the  $\text{NH}_3$ , which will be "fixed" by the HCl.

$\text{NaOH}$ ,  $\text{HNaCO}_3$ ,  $\text{CaO}$ , or  $\text{MgO}$  may be used to set free the  $\text{NH}_3$ , but  $\text{KOH}$  should not be employed on account of the risk of an apparently positive test due to spattering or creeping.

In the routine analysis of material of wholly unknown composition  $\text{NaOH}$  should be used, the use of the other reagents being restricted to examinations of special compounds where it may be desirable to employ a decomposing agent less energetic than  $\text{NaOH}$ . When only a very small amount of  $\text{NH}_3$  is found in the condensate by the procedures described below, it is always essential that a "blank" test be made to assure reagent purity.

Finding  $\text{NH}_3$  in the condensate is not necessarily proof of the presence of the ion  $\text{NH}_4^+$ , since a number of nitrogen-containing organic compounds yield  $\text{NH}_3$  when heated with  $\text{NaOH}$ , especially if an oxidizing substance is also present. In complex mixtures of this sort the identification of ammonium salts is by no means simple and often taxes the ingenuity of the analyst. Usually extraction with warm water and evaporation to crystallization will afford a fairly satisfactory separation of the water-soluble ammonium salts from the generally water-insoluble organic compounds. The identification of the crystalline residue obtained by evaporation may then be undertaken by chemical and optical methods.

Most ammonium salts sublime at moderately low temperatures, and with care satisfactory separations may be thus effected and crystalline sublimates obtained.

In the absence of the reagent  $\text{H}_2\text{PtCl}_6$  it is better to have recourse to  $\text{HIO}_3$  rather than testing with  $\text{Mg}^{++}$  and  $(\text{PO}_4)^{--}$ .

#### Experiments.

(a) Expel  $\text{NH}_3$  from a mixture of  $\text{NH}_4\text{Cl}$  and  $\text{KCl}$ , and test the evolved gas with  $\text{H}_2\text{PtCl}_6$ .

(b) Run a "blank" distillation with  $\text{KCl}$  alone.

(c) Test with  $\text{HIO}_3$  (see Method B).

(d) Repeat the distillation, using urea and  $\text{NaOH}$ , and test for evolved  $\text{NH}_3$ .

#### A. By Means of Chloroplatinic Acid — $\text{H}_2\text{PtCl}_6$ .

*Compound Formed* —  $(\text{NH}_4)_2\text{PtCl}_6$ .

The reagent is applied by Method I, page 31, to the solution of  $\text{NH}_4\text{Cl}$ , obtained by the expulsion of  $\text{NH}_3$  by  $\text{NaOH}$  and fixation in  $\text{HCl}$  in the manner described above.

The  $\text{H}_2\text{PtCl}_6$  test for ammonium is the quickest and most satisfactory at our command. When performed as directed upon expelled  $\text{NH}_3$  it is subject to no errors and few interferences.

The highly refractive, brilliant, clean-cut octahedra grow to a size easily recognized by low powers, and even if the concentration of  $\text{NH}_4\text{Cl}$



in the test drop is so high as to yield skeleton crystals of  $(\text{NH}_4)_2\text{PtCl}_6$ , these skeletons are sufficiently characteristic so that identification is certain. Moreover, recrystallization from hot water is always practicable. On the other hand, if a precipitate is not obtained, recourse to evaporation can always be had.

Although, as pointed out under potassium, the salt  $(\text{NH}_4)_2\text{PtCl}_6$  is less soluble than  $\text{K}_2\text{PtCl}_6$ , the two salts separate from solution on the object slide with exactly the same habit and of substantially the same size. (See Fig. 43, page 69.) The sensitivity of the reaction appears to be substantially the same for both  $\text{NH}_4^+$  and  $\text{K}^+$  ( $0.4 \pm \mu\text{g.}$ ).

For a discussion of the characteristics and relationships of the chloroplatinates, see page 66.

Certain organic compounds that are volatile and water-soluble may appear in the hanging drop and yield a crystalline compound with  $\text{H}_2\text{PtCl}_6$ , but the crystal habit of these compounds is not such as to be confused with  $(\text{NH}_4)_2\text{PtCl}_6$ .

### B. By Means of Iodic Acid — $\text{HIO}_3$ .

#### *Compound Formed* — $\text{NH}_4\text{IO}_3$ .

When ammonium is to be tested for by this method, the  $\text{NH}_3$  is expelled as usual with  $\text{NaOH}$ , but the crucible cover, instead of carrying a drop of  $\text{HCl}$ , is provided with a hanging drop of an approximately 10 per cent solution of  $\text{HIO}_3$ .

The crucible is warmed very gently at intervals, so as to insure a slow expulsion and gradual absorption of  $\text{NH}_3$ , and, as a consequence, the slow growth of the crystals of  $\text{NH}_4\text{IO}_3$  leads to the development of a characteristic habit and dimensions permitting easy recognition.<sup>21</sup>

Although this test is moderately sensitive ( $2 \mu\text{g.}$ ), the formation of characteristic crystals is slow and cannot be hurried.

The crystals of  $\text{NH}_4\text{IO}_3$  (Fig. 52, page 77) usually appear first at the circumference of the hanging drop in the form of more or less dendritic masses made up of colorless, transparent, square, rectangular, or six-sided plates and prisms. The square and rectangular plates have the appearance of belonging to the cubic system but are strongly birefringent, and according to Denigès and to Ries are really monoclinic (pseudo-cubic).<sup>22</sup>

If instead of a 10 per cent solution of  $\text{HIO}_3$  a very concentrated warm solution is employed, a series of acid iodates may be obtained whose composition depends upon conditions; some of these acid salts are

<sup>21</sup> Denigès: *Comptes rend.* 171, 177 (1920).

Denigès and Barlot: *Bul. Soc. Chim.*, (4) 27, 824 (1920).

<sup>22</sup> The *International Crit. Tables* give  $\text{NH}_4\text{IO}_3$  as orthorhombic (Eakle).

metastable. Scratching the slide and breaking up the metastable salts lead to their transformation into stable forms.

Acid iodates of  $\text{Na}^+$  have not been described, but  $\text{NaIO}_3$  and several hydrated salts are known to be orthorhombic. The optical constants of the alkali iodates have not yet been determined.

Unless a definite concentration of the  $\text{HIO}_3$  reagent is adhered to in the study of known and unknown material, confusion may ensue because of the formation and the separation of a series of compounds having different crystal habits and different optical constants.

Since the ion  $\text{IO}_3^-$  yields difficultly soluble crystalline salts with a number of cations, the test for ammonium should never be applied to a solution of the substance but must be made only by exposing a solution of  $\text{HIO}_3$  to the gases expelled by gentle warming with  $\text{NaOH}$ .<sup>23</sup>

**C. Means of Magnesium Acetate —  $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$  and Sodium Phosphate —  $\text{HNa}_2\text{PO}_4$ .**

*Compound Formed* —  $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$ .

To the hanging drop upon the cover-slide obtained as suggested on page 73 (and which presumably contains  $\text{NH}_4\text{Cl}$  in acid solution) add a fragment of  $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ . Stir until all has dissolved. Add a fragment of  $\text{HNa}_2\text{PO}_4 \cdot 12 \text{H}_2\text{O}$ ; stir thoroughly. If a precipitate appears, dissolve in the least possible amount of dilute  $\text{HCl}$ .

Into the test drop thus prepared, cause to flow a drop of  $\text{NaOH}$  of moderate concentration. In the presence of  $\text{NH}_4^+$ , orthorhombic crystals of the salt  $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$  soon make their appearance.

Usually there is first formed a very fine granular or flocculent precipitate. This soon changes into large star-like and X-shaped skeletons that are very characteristic (Fig. 76, page 109). These skeleton crystals in turn disappear by filling out into prismatic types.

In the change from skeleton to prismatic crystals there are formed thin plates with a rhombic or rectangular outline which, as they thicken, assume the appearance of a rectangular or a somewhat distorted envelop; these latter in turn thicken and become prismatic with faces recalling the roofs of houses (Fig. 77, page 109).

If the concentration of the test drop is very low with respect to  $\text{NH}_4^+$ , only the crystals of prismatic habit are seen. In such an event it is best to decant the mother liquor, dissolve the crystalline precipitate in the least possible volume of dilute  $\text{HCl}$ , and into this more concentrated test drop flow the  $\text{NaOH}$ . This procedure is suggested because the skeletons and dendrites passing into the prismatic crystals are the most characteristic phenomena exhibited by  $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$ .

<sup>23</sup> See Detection of the Alkaline Earths, p. 125.

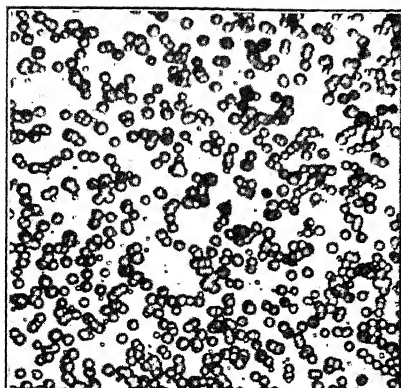


FIG. 48. Rubidium with Sodium Silicomolybdate. 300X.

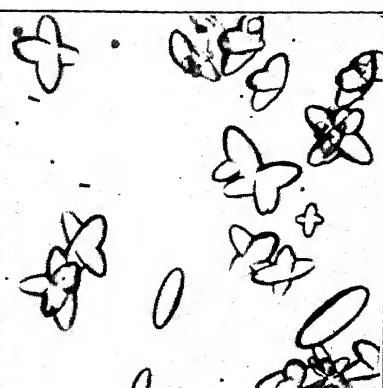


FIG. 49. Lithium with Disodium Phosphate. 200X.



FIG. 50. Lithium with Ammonium Carbonate. 100X.

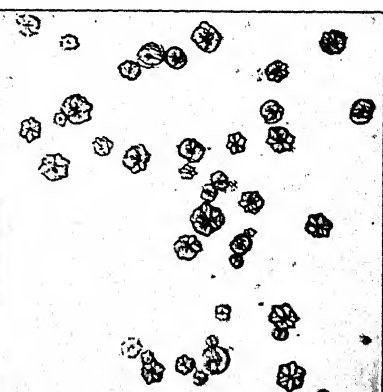


FIG. 51. Lithium with Ammonium Carbonate. 200X.

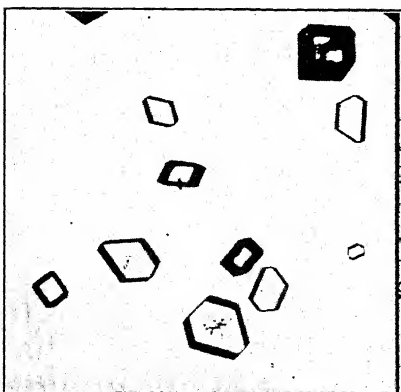


FIG. 52. Ammonium with Iodic Acid. 100X.



FIG. 53. Beryllium with Chloroplatinic Acid. 200X.

## DETECTION OF THE ELEMENTS OF GROUP I

A triclinic salt  $\text{H}_4(\text{NH}_4)_2\text{Mg}_3(\text{PO}_4)_4 \cdot 8 \text{H}_2\text{O}$  has also been described, but it is doubtful whether this salt can appear in the test drop under the conditions which have been outlined above.

In testing for ammonium, there may not be a sufficiently large amount of  $\text{NH}_4\text{Cl}$  present to prevent a separation of  $\text{Mg}(\text{OH})_2$  or of  $\text{Mg}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$ , as heavy flocculent precipitates which fail to crystallize on standing, though in the case of the normal magnesium phosphate the formation of minute monoclinic needles is possible.

Although the salt  $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$  is of little value for the detection of  $\text{NH}_3$  obtained by expulsion with  $\text{NaOH}$ , it is frequently met with by the analyst in plant and animal products, in culture media, etc. It is readily identified by its insolubility in cold water, moderate solubility in boiling water, and its immediate and complete solubility in  $\text{HCl}$ , from which it is reprecipitated by  $\text{NaOH}$  in the crystalline forms described above.

Moreover, this salt is of considerable theoretical as well as practical interest, for it is one of a group of isomorphous salts having the general formula,  $N. M. \text{PO}_4 \cdot 6 \text{H}_2\text{O}$ , in which  $N$  may be  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ , but not  $\text{Na}^+$ ; and  $M$  may be  $\text{Mg}^{++}$ ,  $\text{Fe}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ , and in which  $P$  can be replaced by  $\text{As}$  or  $\text{V}$ .

## DETECTION OF RUBIDIUM AND CESIUM

These two elements differ so little from one another in their chemical behavior and are so closely related to potassium that their microscopical identification in complex mixtures is always exceptionally difficult.

Even when dealing with a relatively pure, simple salt of rubidium or cesium, the differentiation is not easy, since in most tests dependence must be placed upon differences in solubility alone. Attention has already been called to the fact that identity tests based wholly upon differences in solubility require exceptional skill, experience, and judgment on the part of the analyst, and he must form an opinion largely through inference. The microscopical identification of rubidium and cesium in mixtures is therefore always open to more or less uncertainty.

The following reactions may be employed in distinguishing between  $\text{Rb}^+$  and  $\text{Cs}^+$ .

### A. By Means of Potassium Ferricyanide and Lead Acetate.

*Compound Formed* —  $\text{Cs}_3\text{Fe}(\text{CN})_6 \cdot 2 [\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2]$ .<sup>24</sup>

The reagent is prepared by mixing together approximately equal volumes of saturated solutions of potassium ferricyanide and lead acetate. Filter if not clear.

<sup>24</sup> Wenger and Gutzeit: *Manuel de chimie analytique qualitative minérale* (George & Cie, Genève, 1933), p. 93.

To the drop of a neutral or only very faintly acid solution of cesium nitrate add a drop of the reagent by Method I, page 31. The drop to be tested should be concentrated with respect to cesium ions. In a few seconds a crystalline precipitate is formed, consisting of orange or reddish brown square and rectangular plates, singly or in foliated or bristly masses of foliated plates. The plates are usually well formed, have a very characteristic habit, exhibit only very faint pleochroism and weak birefringence. The square plates are biaxial and exhibit symmetrical extinction. The reagent must be in excess (Fig. 58, page 91).

When first appearing the thin plates are yellow by transmitted light, but as they grow thicker they become orange and finally a red-brown. By reflected light on a white background the crystals are brick red.

In dilute solutions no crystals are precipitated, but as the preparation passes to dryness the characteristic plates appear at the periphery of the drop.

This interesting mixed double salt of cesium is difficultly soluble in cold water but readily soluble in hot water, from which it separates on cooling in its original habit, being only partly decomposed when recrystallized by heating the test drop.

Wenger and Gutzeit state that no other known cation yields an orange-colored crystalline precipitate with the reagent. This statement appears to be correct and the test specific for cesium.

With  $\text{TlNO}_3$  the reagent yields no crystalline precipitate at once, but as the test drop begins to pass to dryness there usually appear at its periphery a few scattered, deeply colored, irregular, angular grains and imperfect crystals having tabular, prismatic, or columnar conformations. These more or less dendritic bodies are darker colored than the cesium salt, with an altogether different tint. They are strongly pleochroic and strongly birefringent. They possess an entirely different habit from that of the cesium salt and therefore cannot lead to any confusion. These crystals are probably thallium ferricyanide. (See page 335, ¶ 4.) Mixtures of cesium nitrate and thalious nitrate yield characteristic reactions for cesium.

Rubidium yields no similar compound with the reagent and, even if present in excess of cesium, does not interfere with the detection of cesium.

Cesium ferricyanide-lead acetate forms slowly and usually requires several minutes for its development into its characteristic foliated plates. It is therefore difficult to determine the sensitivity of this test. The test drop may be allowed to pass to dryness without jeopardizing the reliability of the test.

If the test drop contains appreciable amounts of free  $\text{HNO}_3$ , the acid should be driven off by careful evaporation before the reagent solution is added. Sodium or ammonium acetates must not be used to mitigate the action of the acid since both of these acetates inhibit the formation of the cesium compound.

Ions forming insoluble or difficultly soluble reaction products with  $\text{Fe}(\text{CN})_6^{4-}$  or  $\text{Pb}^{++}$  should be absent in the test drop.

In complex mixtures first remove the interfering ions by the Behrens-Schoorl separation method as outlined on page 100, II, using  $\text{HNO}_3$  instead of  $\text{HCl}$ .

### B. By Means of Silver Chloride, $\text{AgCl}$ , and Chloroauric Acid, $\text{HAuCl}_4$ .<sup>25</sup>

*Compounds Formed* —  $6 \text{RbCl} \cdot 2 \text{AgCl} \cdot 3 \text{AuCl}_3$  or  
 $2 \text{CsCl} \cdot \text{AgCl} \cdot \text{AuCl}_3$ .

To a very dilute solution of auric chloride in strong  $\text{HCl}$ , add a small quantity of the material to be tested. Stir thoroughly. If crystals of difficultly soluble chloroaurates appear, dilute the drop and warm gently until the crystals disappear. Into the test drop thus prepared introduce a very little freshly precipitated  $\text{AgCl}$  (or a fragment of  $\text{AgNO}_3$ ). Allow the preparation to stand at room temperature for several minutes, then transfer to the stage of the microscope. If no reaction is obtained, crush a fragment of the material being tested in the center of one of the masses of  $\text{AgCl}$ .

If rubidium is present, the  $\text{AgCl}$  becomes covered with tiny, wine-red, blood red, or brownish-red crystals, but if cesium is present the white masses of  $\text{AgCl}$  become covered with a very fine, jet-black granular film.

Crush the  $\text{AgCl}$  masses, together with the adhering crystals, thus "seeding" the preparation. In a few minutes the chloroaurates will have crystallized throughout the drop.

The cesium silver chloroaurate  $2 \text{CsCl} \cdot \text{AgCl} \cdot \text{AuCl}_3$ <sup>26</sup> is quite insoluble

<sup>25</sup> Emich: *Monats.* 39, 775 (1918); 41, 243 (1920); 46, 261 (1925).

Bayer: *Monats.* 41, 223 (1920).

Vogel: *Monats.* 46, 265 (1925).

Martini: *Mikrochemie.* 8, 231 (1929).

Mellor: *Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longmans, New York), Vol. III, pp. 594-595.

<sup>26</sup> According to Ferrari: *Gazz. Chim. Ital.* 67, 94 (1937), these salts are to be regarded as chloroaurates of  $(\text{AuCl}_6)$  not as triple salts, since they probably have the formulas  $\text{Rb}_2\text{Ag}(\text{AuCl}_6)$  and  $\text{Cs}_2\text{Ag}(\text{AuCl}_6)$ . So cesium chloroaurate is probably  $\text{Cs}_2\text{Au}(\text{AuCl}_6)$ . There is, however, as yet no evidence that the trivalent ion  $\text{AuCl}_6$  exists in solution.

and is therefore mostly precipitated in a very finely divided condition; but, in preparations which have stood for some little time, definite crystals can be found in the form of jet-black squares, hexagons, triangles, and four- and six-pointed stars (Fig. 47, page 69). A magnification of  $200\times$  or over is required to disclose their shape.

The more soluble rubidium salt  $6\text{RbCl}\cdot 2\text{AgCl}\cdot 3\text{AuCl}_3$  makes its appearance after most of the cesium salt has separated. Unlike the cesium salt it crystallizes in well-developed orthorhombic plates and prisms of sufficient size to be readily identified with a 16-mm. objective. The prisms usually have square ends, but sometimes terminate in angles of  $60^\circ$  to  $65^\circ$ . They show a marked tendency to twin and to form masses of radiating slender crystals (Fig. 46, page 69). In color they range from a yellowish-red in thin plates to a deep reddish-mahogany in thick prisms, and may even be so dark as to appear almost black. This compound has a high index of refraction, the crystal faces are brilliant reflecting surfaces and show a play of spectral colors.

This interesting reaction affords an easy method of differentiating between potassium, rubidium, and cesium, providing that comparatively pure salts are dealt with and that ammonium salts are absent.

With salts of ammonium there is often at first obtained a separation of tiny jet-black granules that cannot be distinguished from the cesium reaction. Later orthorhombic prisms appear which in habit and color correspond to the rubidium salt. Wells<sup>27</sup> has shown that the ammonium salt has the formula  $6\text{NH}_4\text{Cl}\cdot 2\text{AgCl}\cdot 3\text{AuCl}_3$ . It is thus similar to the corresponding salt of rubidium.

No crystalline precipitate is obtained with sodium or potassium, but in concentrated solutions the  $\text{AgCl}$  may become peptized and turn black in such a manner as to necessitate very careful observation to avoid falling into the error of concluding that cesium is present.

Even if the preparation is allowed to stand until the test drop has evaporated to dryness, the double chloroaurates are still easily differentiated. The cause of the color of these compounds has not yet been satisfactorily accounted for.

If the solution of  $\text{AuCl}_3$  is not sufficiently dilute, simple chloroaurates are apt to separate in crystalline form. This is especially true of the alkali chloroaurates; the solubilities of these salts expressed in grams per 100 grams of water at  $20^\circ$  are as follows:  $\text{Li}^+$  57.7;  $\text{Na}^+$  60.2;  $\text{K}^+$  38.2;  $\text{Rb}^+$  9.0;  $\text{Cs}^+$  0.8. It is obvious that in testing by this method simple chloroaurates are almost sure to be precipitated as well as the double chloroaurates.

Calcium, strontium, and barium form chloroaurates of the general

<sup>27</sup> Wells: *Amer. Jour. Sci.* (5) 3, 315 (1922); (5) 4, 476 (1922).

formula  $M(\text{AuCl}_4)_2 \cdot 6 \text{H}_2\text{O}$ ; the Mg group yields  $M(\text{AuCl}_4)_2 \cdot 12 \text{H}_2\text{O}$  or  $M(\text{AuCl}_4)_2 \cdot 8 \text{H}_2\text{O}$ ;  $\text{Mn}^{++}$  gives  $\text{Mn}(\text{AuCl}_4)_{12} \cdot \text{H}_2\text{O}$  or  $\text{Mn}(\text{AuCl}_4)_2 \cdot 8 \text{H}_2\text{O}$ ,  $\text{Co}^{++}$  and  $\text{Ni}^{++}$   $M(\text{AuCl}_4)_2 \cdot 8 \text{H}_2\text{O}$ . The crystallography of none of these compounds has been definitely established.

By substituting I for Cl in the gold reagent there is obtained iodoauric acid, which has been shown to yield specific reactions for the potassium group of metals.<sup>28</sup>

If a drop of a mixture of  $\text{HAuI}_4$  and  $\text{AgI}$  in  $\text{HI}$  is caused to flow into a test drop containing members of the potassium group, there will be formed double iodoaurates of as yet unknown composition. The potassium salt separates as black, slender, acicular crystals, singly and in groups and bundles. Ammonium gives black, curving, brush-like aggregates that soon disintegrate. Rubidium forms black, irregular, four-sided plates, and cesium yields black vermiform aggregates, crosses, rods, and hexagons.

Unfortunately the reagent necessary for these interesting reactions is not easily prepared and is very unstable; hence the test is impracticable in routine qualitative analysis.

If instead of  $\text{HAuCl}_4$ , chlorostannic acid  $\text{H}_2\text{SnCl}_6$  and  $\text{AgCl}$  are used, very insoluble chlorostannates of silver and rubidium and cesium are obtained; and in this case the difference in the solubilities of the rubidium and cesium salts appears to be even greater than in the case of the gold salts. Unfortunately, these reactions cannot be used to good advantage in microscopical qualitative analysis.

## TESTS WITH HETEROPOLY ACIDS

### C-1 By Means of Silicotungstic Acid<sup>29</sup> — $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 5 \text{H}_2\text{O}$ .

*Compounds Formed* —  $\left. \begin{array}{l} \text{Rb}_3\text{HSiW}_{12}\text{O}_{40} \\ \text{Cs}_3\text{HSiW}_{12}\text{O}_{40} \end{array} \right\} ?$

To the very dilute solution to be tested, made strongly acid with  $\text{HCl}$ , add a concentrated solution of the reagent by Method I, page 31. Cesium is instantly precipitated in a sandy or granular mass, which even under moderately high magnifications shows no definite crystal form other than minute disks or rounded grains which are pure white by reflected light but black by transmitted light. If the test drop is sufficiently dilute, the rubidium salt will not be precipitated at once but

<sup>28</sup> Burkser and Rublof: *Mikrochemie* 5, 137 (1927).

Gravestein: *Emich-Festschrift, Mikrochemie*, p. 140, suggests using  $\text{AgI}$  in  $\text{NaI}$  as a specific test for Cs.

<sup>29</sup> O'Leary and Papish: *Ind. Eng. Chem. Anal. Ed.* 6, 107 (1934); Illingworth and Keggins: *Jour. Chem. Soc.* 1935 (I), 575.



appears in a short time as small disks and spheres many times larger than those of cesium.

Potassium, ammonium, and sodium separate from concentrated solutions only.

Thallium ( $Tl^+$ ), however, is precipitated under the same conditions as cesium; but, since thallos chloride is difficultly soluble and its crystal habit is quite characteristic, there is no danger of confusing thallium with cesium.

Because of the great difference in the solubilities of rubidium and cesium silicotungstates, it is possible to detect these elements in the presence of each other by testing a series of drops of greatly decreasing concentrations. Nevertheless, care, skill, and practice are required in all dilution tests of this nature.

Silicotungstic acid yields precipitates with many cations other than those of the alkali group; hence tests for rubidium and cesium should be made upon material which has been submitted to some separation method whereby these interfering ions have been removed. (See pages 99-100.)

If the alkali residue obtained as the result of a separation method still contains a relatively large amount of lithium (which may happen when the separation has been incomplete), there may be formed, as the preparation passes to dryness, colorless hexagons and bipyramidal prisms, of the hexagonal system, of lithium silicotungstate, probably  $Li_3HSiW_{12}O_{40} \cdot nH_2O$ .

## C-2. By Means of Ammonium Silicomolybdate —



The difference in the solubilities of the silicomolybdates of rubidium and cesium is sufficiently great to permit differentiation by having recourse to the dilution method discussed under *E* (page 86).

The most satisfactory results appear to be obtained when the reagent is applied by Method III, page 35. The dry film should be *exceedingly thin* and prepared from an *excessively* dilute solution. The reagent consists of a dilute solution of ammonium silicomolybdate acidified with a trace of  $HNO_3$ . This very dilute solution is drawn across the dry film and then *at once* a drop of a concentrated solution of the reagent is added in the same place and the object slide slightly tilted so as to cause the concentrated reagent to flow into the channel and across the test drop.

If rubidium is present, there will appear, along the edges of the channel, tiny, lemon-yellow, darkly contoured, spherical crystals some-

<sup>30</sup> Illingworth and Keggins: *op. cit.*

times resembling octahedra and cubes with more or less rounded angles. Most of these crystals appear to be spheroidal and their crystal faces can be discerned only by careful illumination and focusing (Fig. 48, page 77). Tiny, three-, four-, and six-armed skeletal crystals are also formed in abundance. The composition of this salt has not been established definitely.

In the case of cesium salts tested in this manner, only a very fine granular precipitate is obtained. Even high magnifications fail to reveal more than rounded grains and minute disks.

The potassium salt is quite soluble and may appear as well-formed prisms of considerable size. The salts of sodium and lithium are too soluble to separate under the conditions of the test.

$\text{Ag}^+$ ,  $\text{Tl}^+$ , and  $\text{Hg}^+$ , and also the ions of the magnesium and the calcium groups yield difficultly soluble silicomolybdates; but, if the test has been performed as described, these ions will not interfere with the identifications of rubidium and cesium.

Better-formed crystals of rubidium silicomolybdate can be obtained by adding a dilute solution of the reagent to a dilute solution of the rubidium salt, but this method of testing does not yield as sharp a differentiation between rubidium and cesium.

The presence in the test drop of a moderate concentration of ammonium salts is objectionable, as there is then danger of the separation of crystals of an  $\text{NH}_4$  salt of uncertain composition.

#### D. By Means of Chlorostannic Acid — $\text{H}_2\text{SnCl}_6$ .

*Compounds Formed* —  $\text{Rb}_2\text{SnCl}_6$  or  $\text{Cs}_2\text{SnCl}_6$ .

When tin is dissolved in  $\text{HCl}$  and the solution boiled in the presence of oxygen (air),  $\text{SnCl}_4$  is formed; and, if an excess of strong  $\text{HCl}$  is present, we may regard the compound present in solution as  $\text{H}_2\text{SnCl}_6$ . This constitutes the reagent for members of the potassium group.

The reagent should be added to very dilute test drops only. Acidification with  $\text{HCl}$  is desirable, and the best results are obtainable when the reagent is added by Method I, page 31.

Freshly prepared solutions of  $\text{H}_2\text{SnCl}_6$  are preferable to solutions obtained by dissolving crystalline  $\text{SnCl}_4$  in water.<sup>31</sup>

Cesium is instantly precipitated as  $\text{Cs}_2\text{SnCl}_6$  in the form of very tiny, colorless, highly refractive, regular octahedra and cubes (Fig. 122, page 183). The salt is so difficultly soluble that even in very dilute

<sup>31</sup> Stannic chlorides of commerce are usually mixtures. They correspond to the formula  $\text{SnCl}_4 \cdot x\text{H}_2\text{O}$ , where  $x$  may be 3, 5, or 8. All three salts are monoclinic. Old samples of stannic chloride are usually basic and do not dissolve completely in dilute  $\text{HCl}$ . Such samples should be heated with aqua regia, the excess of acid driven off, and the resulting clear solution employed as reagent.

solutions the crystals formed usually require a magnification of at least  $200\times$  for their resolution. Not infrequently  $\text{Cs}_2\text{SnCl}_6$  is precipitated as masses of skeleton crystals. Under these conditions the crystals are very much larger and cannot be distinguished from skeleton crystals of  $\text{Rb}_2\text{SnCl}_6$ . Skeleton crystals are not formed if the dilution of the test drop has been sufficiently great.

$\text{Tl}_2\text{SnCl}_6$  is even less soluble than  $\text{Cs}_2\text{SnCl}_6$  and is therefore always precipitated in exceedingly minute cubes, octahedra, or in skeletal forms. The crystals are colorless and highly refractive.

$\text{Rb}_2\text{SnCl}_6$  also forms colorless octahedra, but because of the higher solubility of the salt the crystals are much larger than those of cesium.

$\text{K}_2\text{SnCl}_6$  forms relatively large, colorless octahedra whose solubility is so much greater than that of either  $\text{Cs}_2\text{SnCl}_6$  or  $\text{Rb}_2\text{SnCl}_6$  that there is little danger of confusing potassium with rubidium or with cesium; but, if much strong  $\text{HCl}$  is present, differentiation becomes impossible. The ammonium salt differs but little from the potassium salt in solubility.

The chlorostannate of sodium and that of lithium are so soluble that they will not appear until the test drop passes to dryness. Both these salts are hydrated, and of uncertain composition. Neither one crystallizes in the cubic system.

Thus far, anhydrous chlorostannates only have been prepared of ammonium, rubidium, and cesium. But potassium forms  $\text{K}_2\text{SnCl}_6 \cdot \text{H}_2\text{O}$  (orthorhombic) below  $25^\circ \text{C}$ .; above  $25^\circ \text{C}$ . the anhydrous salt is formed, nevertheless at room temperature upon an object slide the anhydrous salt separates. The potassium salts readily hydrolyze if boiled in concentrated solutions containing little or no free  $\text{HCl}$ .

All attempts to prepare crystalline chlorostannates of  $\text{Ag}^+$ ,  $\text{Cu}^+$ , or  $\text{Au}^+$  have thus far failed.

The difference in the solubilities of the cesium and rubidium chlorostannates is sufficiently great to enable an experienced analyst to distinguish between them, especially if the dilution method described on pages 83, 86 is followed.

Ammonium salts should be absent; they can be removed by ignition or treatment with  $\text{NaOH}$ .

The sensitivity of the reaction can be increased by adding to the test drop a fragment of  $\text{NaI}$ , thus causing the formation of yellow iodostannates. The yellow-colored salt is believed to be due to the formation of a solid solution of  $\text{Cs}_2\text{SnI}_6$  in  $\text{Cs}_2\text{SnCl}_6$ .

In the presence of much  $\text{Fe}^{+++}$  the chlorostannates are colored yellow.

For a further discussion of the chlorostannates and allied salts, see Tin, page 201.

Since the reagent contains  $\text{Cl}^-$  ions, any compounds present precipitable by  $\text{Cl}^-$  will separate in the test drop unless  $\text{HCl}$  has been added

to the solution of the unknown before the application of the chlorostannic acid. Silver, unless removed, may under favorable conditions yield colorless highly refractive cubes and octahedra of  $\text{AgCl}$ . For other possible compounds appearing as precipitates when  $\text{HCl}$  is added, see page 394.

**E. By Observation of the Differences in the Solubilities of  $\text{Rb}_2\text{PtCl}_6$  and  $\text{Cs}_2\text{PtCl}_6$ .**

The solubility of the different alkali chloroplatinates rapidly decreases with the rise in the atomic weight of the cation.

If a drop of a concentrated solution of  $\text{H}_2\text{PtCl}_6$  is caused to flow into an exceedingly dilute solution of salts (chlorides) of the alkali metals,  $\text{Rb}_2\text{PtCl}_6$  and  $\text{Cs}_2\text{PtCl}_6$  will be almost instantly precipitated as skeletal crystals or as minute octahedra; but crystals of corresponding salts of potassium or ammonium will not appear until the concentration is very much higher and the sodium salt will not separate until the preparation passes substantially to dryness.

The size of the crystals formed and the limiting values for their almost instantaneous precipitation offer a method for differentiating between potassium, rubidium, and cesium. The elimination of potassium from the problem is fairly simple by comparing the behavior of the unknown material with "blank" tests containing  $\text{KCl}$ . If to a series of test drops of varying concentrations of the unknown and drops of  $\text{KCl}$  of as nearly as possible the same concentration and degree of acidity (with  $\text{HCl}$ ), in each different set of drops,  $\text{H}_2\text{PtCl}_6$  is added, and a precipitation of tiny yellow octahedral crystals is obtained in the drops of the unknown *after* the corresponding dilution drops of  $\text{KCl}$  have failed to yield a separation of chloroplatinate crystals, and the crystals obtained with the unknown are *smaller* than experience has shown are to be expected with potassium, the assumption is justified that rubidium or cesium (or a mixture) is present and not potassium.

The same method of procedure may then be adopted to differentiate between rubidium and cesium.

This method of attack (which is Method IV, page 37) may often be applied to mixtures with good results; but it must be borne in mind that if, in the drops of the solution of the unknown, there are materials which will affect the solubility or alter the characteristic habit of the alkali chloroplatinates, the results of the test are valueless so far as identification of the cation is concerned.

The differentiation between  $\text{Cs}^+$  and  $\text{Tl}^+$  is not possible by this method.

A variant of the above "dilution" method consists in adding to the test drop a drop of a saturated solution of  $\text{K}_2\text{PtCl}_6$ , on the principle that this reagent will not cause a precipitate in a *dilute* solution containing  $\text{K}^+$ , but an immediate precipitate will result if  $\text{Rb}^+$  or  $\text{Cs}^+$  (or  $\text{Tl}^+$ ) is present.<sup>32</sup>

## DETECTION OF LITHIUM

The microscopical identification of lithium is practicable only in materials in which lithium is present in relatively high concentrations. This restricts the application of the tests to comparatively pure salts.

<sup>32</sup> See Gravestien: *Emich-Festschrift*, p. 135 (*Mikrochemie*, 1930).

very simple mixtures, or to material in which lithium has been concentrated by extraction and separation methods, *e.g.*, conversion into chloride or bromide, and extraction of the dry residue with one of the higher alcohols in which LiCl is quite soluble, but in which most other chlorides and bromides are difficultly soluble or quite insoluble.

Lithium is best identified by the flame spectrum of its chloride  $\text{Li}\alpha = \lambda 6708$ .

Not only have we no good chemical tests for this element, but there are few salts of lithium that crystallize sufficiently well to permit a satisfactory determination of their optical constants when crystallized upon an object slide.

Lithium can be differentiated from the alkali metals in that it forms a difficultly soluble phosphate and carbonate. Its easily soluble sulphate readily distinguishes it from the sulphates of the alkaline earths.

The salts of lithium, as a general rule, resemble those of sodium more than those of the other alkali metals, in that the perchlorate, chloroplatinate, chlorostannate, tartrate, triple chloride (Li, Ag, Au), picrate, and silicomolybdate are all so soluble as not to separate under the conditions which obtain in the testing for members of the potassium group.

Unlike sodium, lithium yields no double acetate of low solubility with  $\text{UO}_2^{++}$ , nor does it form a difficultly soluble double sulphate with bismuth. Its fluosilicate is more soluble than that of sodium, and it is almost impossible to induce lithium to form an "alum" upon an object slide.

The relatively low solubility of lithium carbonate and of lithium phosphate throws lithium into Group II with the alkaline earths. But lithium differs from magnesium in that its double phosphate with ammonium  $\text{NH}_4\text{Li}_2\text{PO}_4 \cdot 6\text{H}_2\text{O}$  is soluble in ammoniacal solutions. Unlike calcium, strontium, and barium, the sulphates and oxalates of lithium are quite soluble.

All the above facts relative to the analytical behavior of lithium must be borne in mind whenever analyses are to be made of materials in which lithium may possibly be present.

Lithium is co-precipitated with sodium by the bivalent uranyl acetates. (See Na, page 56.)

#### A. Identification by Means of Disodium Phosphate —



*Compound Formed* —  $\text{Li}_3\text{PO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ .

The solution to be tested should be concentrated with respect to lithium and must be neutral, or better, very slightly alkaline. The reagent is added by Method I, page 31, and the preparation heated

almost to boiling. A granular precipitate of  $\text{Li}_3\text{PO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$  appears at once. This precipitate when examined at  $200\times$  is seen to consist of highly refractive lenticular and fusiform crystals, singly or in crosses or in star-like groups or irregular radiating clumps (Fig. 49, page 77). Sheaves, bundles, and more or less spherical masses of exceedingly fine crystals are sometimes formed. The fusiform and acicular crystals extinguish in the direction of their elongation. The spherulites show the usual black cross between crossed nicols. This salt is dimorphic, forming crystals belonging either to the orthorhombic system or to the hexagonal system.

Only the fusiform crystals are to be regarded as characteristic of lithium.

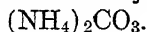
If the solution to be tested is acid, evaporate to dryness to drive off the excess of acid, then neutralize with *very dilute*  $\text{NaOH}$ , using great care *not to exceed* a mere trace of alkalinity. Neutralization by means of  $\text{NH}_4\text{OH}$  is to be avoided since the salt  $\text{NH}_4\text{Li}_2\text{PO}_4 \cdot 6 \text{H}_2\text{O}$  is apt to be formed, thus preventing the precipitation of tri-lithium phosphate; for the same reason ammonium salts should be absent.

It is therefore important that a test for the presence of ammonium ( $\text{NH}_4$ ) shall be made before testing for lithium. If  $\text{NH}_4^+$  is found, drive it off by ignition or by expulsion with  $\text{NaOH}$ .

Because a specific microscopical test for lithium has not yet been found it is necessary to separate the lithium ion in a relatively pure state if its identification is possible. This is usually accomplished by extraction with an alcohol or other organic solvent. But, if the salts to be subjected to the extraction process contain nitrates, the lithium-containing extract may have a sufficient amount of other cations to interfere seriously with the detection of lithium.

The ready solubility of  $\text{NH}_4\text{Li}_2\text{PO}_4 \cdot 6 \text{H}_2\text{O}$  may be turned to good account when doubtful tests are obtained. The supernatant liquid is decanted from the precipitated phosphate (or filtered), the residue is washed, and then dissolved in the least possible amount of very dilute  $\text{HCl}$ . To this clear solution,  $\text{NH}_4\text{OH}$  is added. If no precipitate appears, the precipitate may have been lithium phosphate; but, if a precipitate appears, members of Group II or other groups higher in the periodic series are present.

#### B. Identification by Means of Ammonium Carbonate —



*Compounds Formed.* —  $\text{Li}_2\text{CO}_3$ .

Add the reagent by Method II, page 33, to a neutral solution of the material to be tested. As in all tests for lithium, the drop must be concentrated with respect to this element.

$\text{Li}_2\text{CO}_3$  is not precipitated at once, but after a few minutes separates in the form of globulites, bristly masses, and sheaf-like bundles of acicular monoclinic crystals. More or less irregular thin plates are also formed. All these crystals, especially the aggregates, vary with the concentration of the test drop (Figs. 50, 51, page 77). Hence care and experience are required both in judging the proper concentration and in the interpretation of the results obtained. When in doubt, perform a test upon a known lithium salt, duplicating the conditions, as far as possible, in the "blank" and the test drop.

This reaction is characteristic only when applied to comparatively pure salts of lithium. It is generally unsatisfactory and unreliable when applied to complex mixtures.

Calcium is precipitated in tiny, sparkling, strongly birefringent disks and rhombs, which cling tightly to the glass of the object slide and permit easy decantation of the mother liquor and subsequent identification of the crystals by other reagents. The crystals of  $\text{CaCO}_3$  are usually hexagonal rhombohedral, but are sometimes orthorhombic.

Strontium yields spherulites of  $\text{SrCO}_3$ , often of considerable size; these spherulites are usually incompletely filled out, producing sheaf-like or dumb-bell aggregates.

Barium forms tiny spherulites, fusiform bundles, and sheaf-like aggregates not readily distinguished from the similar aggregates of strontium.

In the high concentrations required for the separation of  $\text{Li}_2\text{CO}_3$ , the alkaline earths give only fine granular precipitates, the forms just described being absent.

$(\text{NH}_4)_2\text{CO}_3$  is used as reagent rather than  $\text{HNaCO}_3$  so as to avoid the separation of the zinc double salt (see Zinc, page 145) or the formation of a double sodium calcium carbonate.

One of the most serious drawbacks of the carbonate test for lithium is that the concentrations required are so high that many salts are apt to crystallize in the test drop, thus masking the lithium test. Moreover, it is very difficult so to control conditions that only  $\text{Li}_2\text{CO}_3$  is formed. No less than eleven hydrated carbonates of  $\text{Li}_2\text{CO}_3$  have been described, but it is probable that many of these are mixtures. The salt  $\text{HLiCO}_3$  exists in solution only.

Magnesium interferes seriously with the carbonate test for lithium or the alkaline earth, and it is to be expected that the test may fail in the presence of any element yielding an insoluble or difficultly soluble carbonate or forming an insoluble hydroxide.

Under certain conditions the crystals of  $\text{Li}_2\text{CO}_3$  bear a striking resemblance to sheaves of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Both are monoclinic. Since

$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  is much more soluble in acid than in neutral or alkaline solution, it may happen that the addition of  $(\text{NH}_4)_2\text{CO}_3$  may cause a precipitation of  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  in bundles of fine acicular crystals.

### OTHER TESTS FOR MEMBERS OF GROUP I

The following tests, although of very little value in the analysis of complex materials of the sort which commonly come to chemists for examination, may nevertheless be of considerable value in special cases.

Since these tests are limited in their application, only a brief description is given of each.

#### Sodium, by Means of Potassium Antimonate — $\text{K}[\text{Sb}(\text{OH})_6]$ .

*Compound formed* —  $\text{Na}[\text{Sb}(\text{OH})_6]$ .<sup>33</sup>

Apply a saturated solution of the reagent by Method I, page 31, to a neutral, moderately concentrated test drop.<sup>34</sup>

Small fusiform crystals are precipitated or thin elliptical plates, uniting in crosses, stars, or globular masses (Fig. 39, page 61). From dilute solutions, non-characteristic tetragonal tetrahedra, cubes, and octahedra separate. No precipitate is obtained with  $\text{Rb}^+$ ,  $\text{Cs}^+$ , or  $\text{NH}_4^+$  but much  $\text{NH}_4^+$  interferes.  $\text{Li}^+$  and  $\text{Mg}^{++}$  give hexagons (Fig. 40, page 61). Alkaline earths and many heavy metals give rise to "amorphous" precipitates.

#### Experiments.

(a) Try the reaction with potassium antimonate on salts of Na in both dilute and concentrated solutions.

(b) Try the reagent on  $\text{NH}_4$  salts alone and then in a mixture of Na and  $\text{NH}_4$  salts.

(c) Try the reagent on a salt of Mg; a salt of Ba.

#### Potassium, by Means of Picric Acid — $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH}$ .

*Compound Formed* —  $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OK}$ .

Apply an alcoholic solution of the reagent by Method V, page 38.

Long, yellow, characteristic, acicular crystals or long, tapering, prism-like forms are obtained. The reagent is dissolved in dilute alcohol and sufficient water added to prevent the drops, when placed on the object slide, from flowing over the glass.

Picric acid crystallizes in orthorhombic prisms very different from those of the potassium salt.

<sup>33</sup> L. Pauling: *Jour. Amer. Chem. Soc.* 55, 1895, 3052 (1933), has shown that these salts long miscalled "pyroantimonates" are in reality salts of a monobasic hydrous antimonous acid of the probable composition  $\text{H}[\text{Sb}(\text{OH})_6]$ .

<sup>34</sup> See also Böttger: *Pregl-Festschrift*, p. 16 (*Mikrochemie*, 1929).



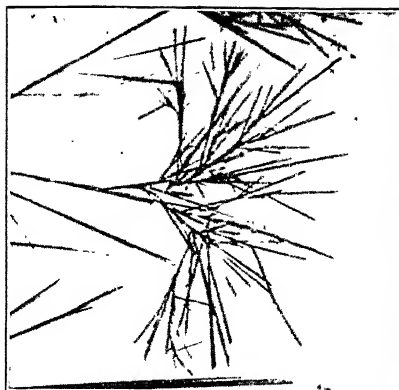


FIG. 54. Cesium with Hexanitrodiphenylamine. 100X.



FIG. 55. Cesium with Hexanitrodiphenylamine. 100X.



FIG. 56. Potassium with Hexanitrodiphenylamine. 100X.



FIG. 57. Potassium with Hexanitrodiphenylamine. 100X.



FIG. 58. Cesium with Lead Acetate and Potassium Ferricyanide. 100X.

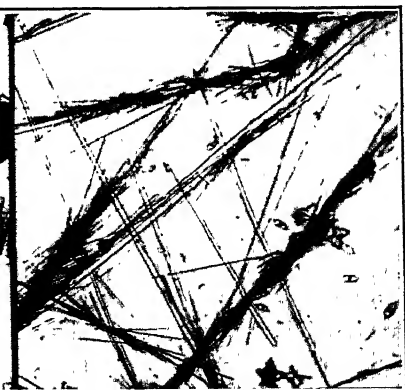


FIG. 59. Sodium with Nitrobarbituric Acid. 20X.

The sodium and lithium salts are too soluble to give a reaction. But, if the preparation is allowed to stand and pass to dryness, characteristic crystals of sodium picrate separate in radiates and sphero-crystals of very fine yellow needles which are readily differentiated from the picrates of the other alkalis.<sup>35</sup>

Rubidium and cesium give crystals closely resembling those of potassium. Ammonium may yield long acicular crystals but more often long thin plates; these crystals may be either yellow or reddish; the latter are strongly pleochroic.  $\text{TI}^+$  behaves like  $\text{K}^+$  but the crystals are smaller; a yellow and a red form are known.

If to a drop of a concentrated aqueous solution of picric acid there is added a good-sized fragment of the salt to be tested, this *fragment* soon bristles with crystals of the picrate of the cation present.<sup>36</sup> These crystals differ sufficiently in appearance, in the case of many cations, to enable an experienced analyst to differentiate between them, but are useful only when dealing with single salts or simple mixtures.

In various modifications picric acid has been suggested as a useful reagent for the detection of: Alkali Group;  $\text{Ag}^+$ ,  $\text{Al}^{+++}$ ;  $\text{Au}^{+++}$ ;  $\text{Ba}^{++}$ ;  $\text{Ca}^{++}$ ;  $\text{Cd}^{++}$ ;  $\text{Co}^{++}$ ;  $\text{Cu}^{++}$ ;  $\text{Fe}^{+++}$ ;  $\text{Hg}^{++}$ ;  $\text{Mg}^{++}$ ;  $\text{Mn}^{++}$ ;  $\text{Ni}^{++}$ ;  $\text{Pb}^{++}$ .

The extensive use of picrates in percussion and other explosives is sufficient justification for the inclusion of picric acid as a reagent since microscopical analytical methods are usually the most satisfactory for the qualitative analysis of these products.

Picric acid also forms crystallizable picrates with a large number of organic compounds; hence the usefulness of this reaction for the potassium group is greatly restricted.

**Potassium, by Means of Sodium Cobaltinitrite** —  $\text{Na}_3\text{Co}(\text{NO}_2)_6$ .

*Compound Formed* —  $\text{K}_3\text{Co}(\text{NO}_2)_6 \cdot 1\frac{1}{2} \text{H}_2\text{O}$  or  $\text{NaK}_2[\text{Co}(\text{NO}_2)_6]$ .

Apply a solution of sodium cobalt nitrite by Method I, page 31. An exceedingly fine granular precipitate is formed, too finely crystalline to be of value in the analysis of complex mixtures.  $\text{NH}_4^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  give a like reaction.

**By Means of the Triple Nitrite Reaction**, see Lead, page 207.

**By Means of Chlorostannic Acid** —  $\text{H}_2\text{SnCl}_6$  — see page 84.

**Lithium, by Means of Ammonium Fluoride** —  $\text{NH}_4\text{F}$ .

Lithium fluoride crystallizes in cubes and other forms of the cubic systems. This reaction is not characteristic, but because  $\text{LiF}$  is less soluble than  $\text{NaF}$  or  $\text{KF}$  the reaction is a useful one.

<sup>35</sup> Denigès: *Bul. trav. soc. pharm. Bordeaux*. 71, 191 (1933).

<sup>36</sup> Frangopol: *Bul. soc. romane chim.* 37, 259 (1934).

**The Alkalis, by Means of 2',4',6',-2,4,6-Hexanitrodiphenylamine<sup>37</sup>**  
(Dipicrylamine, Hexamine) —  $(\text{O}_2\text{N})_3\cdot\text{C}_6\text{H}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$ .

*Compounds Formed* —  $(\text{M})^+\text{N}\cdot[\text{C}_6\text{H}_2(\text{NO}_2)_3]_2$ .

The hydrogen in the amine group has acidic properties and can be replaced by many cations.

The reagent is prepared by adding to a small fragment of NaOH dissolved in a few drops of water *an excess* of purified hexanitrodiphenylamine. Warm gently, and after cooling to room temperature filter the deep orange-red solution.<sup>38</sup>

The test drop should be exceedingly dilute and neutral or at the most only very slightly acid. The orange-colored reagent is best added by Method I or Method IA, page 32. If members of the potassium group are present, an almost immediate sandy precipitate is formed from which characteristic crystals develop. If the concentrations of test drop and of reagent have been properly adjusted, the following phenomena should be observed.

With potassium, dark red-brown dendrites made up of *angular* grains arranged in crosses, X's, or many-branched masses; the latter when made up of very minute grains may appear almost moss-like. On standing for a time, elongated six-sided *ribbed* plates appear. These characteristic plates or plate-like prisms, when thin, are light yellow; when thick, orange or reddish by transmitted light. Usually small orange rhombs and rhomboidal forms also occur (Figs. 56, 57, page 91).

Ammonium yields crystal forms closely resembling those obtained with potassium, but there is a greater tendency toward orange tablets and prisms and far less formation of dendrites made up of angular grains. The difference is sufficiently marked to enable an experienced analyst to differentiate between  $\text{NH}_4^+$  and  $\text{K}^+$  in simple salts but not in mixtures.

Rubidium separates in mossy rosettes, small crosses in X's, the latter usually with curving arms. Short plates and tablets with blunt ends are also to be found. The majority of the crystals in every field are

<sup>37</sup> Poluektor: *Mikrochemie* 14, 265 (1934).

Van Nieuwenburg and Van der Hoek: *Mikrochemie* 18, 175 (1935).

Sheintzis: *Chem. Abs.* 30, 1691 (1935).

<sup>38</sup> The reagent thus prepared is more dependable than the commercial dye Aurantia. This dye, as marketed, may be either the ammonium or the sodium salt of the amine. It is essential that the reagent used for testing for members of the potassium group shall be free from ammonium. The amine can be prepared from the commercial dye by dissolving the Aurantia in a small amount of distilled water and adding thereto strong nitric acid. The precipitated yellow crystalline, hexanitrodiphenylamine is separated from the acid, washed with cold dilute nitric acid and ice water, and the product thus obtained air-dried.

distinctly different from those formed by potassium and ammonium, but unfortunately these are accompanied by crystal forms identical with those of potassium and ammonium.

Cesium forms masses of hair-like crystals or long needles arranged like fans (Fig. 54, page 91). These acicular crystals may develop into very long slender prisms (Fig. 55, top, page 91). On standing, thin four-sided yellow plates, with one or both ends oblique, appear; these may develop into orange tablets or short stout prisms. The six-sided ribbed plates characteristic of potassium are absent (Fig. 57, page 91).

Thallium is precipitated as a reddish salt, black by transmitted light; granular at first but rapidly changing into well-defined prismatic grains. Later, tiny thin yellow rhombs appear and elongated hexagonal plates which are not ribbed. Unless the test drop is exceedingly dilute, there is danger of confusing  $\text{Cs}^+$  and  $\text{Tl}^+$ .

In mixtures of  $\text{K}^+$  and  $\text{Cs}^+$  or  $\text{K}^+$  and  $\text{Tl}^+$  it is possible to identify both in the same test drop, but  $\text{Cs}^+$  and  $\text{Tl}^+$  occurring together cannot be differentiated by this reagent.

Lithium yields no immediate reaction, but on standing very tiny, slender X's with delicate dendritic branches may appear. Lithium does not interfere with the detection of the potassium group.

$\text{Ca}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Mn}^{++}$ , give no apparent reactions in dilute solutions, nor do they interfere with the detection of the potassium group.

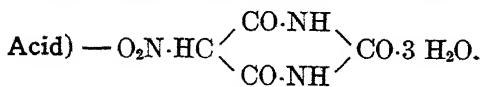
$\text{Be}^{++}$ ,  $\text{Al}^{+++}$ ,  $\text{Ga}^{++}$ ,  $\text{In}^{+++}$ , all yield very tiny stars, X's, irregular angular grains, or fusiform crystals. The crystals formed by  $\text{Be}^{++}$  are much larger than those of the other members of this group.

$\text{Zn}^{++}$ ,  $\text{Cd}^{++}$ , yield no immediate reaction.  $\text{Hg}^{++}$  behaves in like manner but  $\text{Hg}^+$  forms tiny crosses and X's.

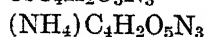
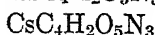
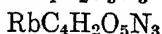
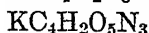
$\text{Pb}^{++}$  forms an orange-red or crimson precipitate consisting of tiny angular grains and disks. The color of the precipitate appears to be specific for lead.

$\text{Ni}^{++}$  and  $\text{Co}^{++}$  yield no apparent reaction, but non-characteristic precipitates may appear on standing.

The Alkalis, by Means of 5-Nitrobarbituric Acid<sup>39</sup> (Dilituric



Compounds Formed —  $\text{NaC}_4\text{H}_2\text{O}_5\text{N}_3 \cdot 2 (?) \text{H}_2\text{O}$



<sup>39</sup> Fredholm: *Zeit. anal. Chem.* 104, 400 (1936).

To a neutral, or at the most only very slightly acid, test drop, add a dilute solution of the reagent<sup>40</sup> by Method I, or better Method IA, page 32.

Sodium yields very long slender prisms which may be acicular or hair-like; they are strongly birefringent with polarization colors of the first and second orders and exhibit oblique extinction. In dilute solutions the sodium salt does not separate at once but appears on standing. If the concentration of the test drop in  $\text{Na}^+$  is moderately high, there is an immediate precipitation of slender prisms in sheaves and imperfect radiates which may closely resemble those of  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ . The test for sodium usually fails in the presence of the other members of Group I unless sodium is in great excess.

To obtain satisfactory crystals with the other members of Group I, the test drop must be exceedingly dilute, since the solubilities of the salts formed are all very low.

Potassium yields difficultly soluble, strongly birefringent, tiny grains with angular outlines, tiny tablets of somewhat rhomboidal form bounded by heavy black contours, thin blades with curving sides, many of them resembling a drawn-out section mark (§) or greatly elongated letter -S-. The chief habit of all the nitrobarbiturates of the potassium group is that of double wedges with bases end-to-end. As seen in one orientation, the ends are very thin and may be bent. When lying flat, not edgewise, the crystals are therefore much thicker at the middle and thin at the ends; the polarization phenomena exhibited therefore are curious and characteristic of these salts. Extinction is oblique. When the reagent is applied by Method IA, the most characteristic habit of the potassium salt appears to be that shown in Figs. 60 and 61, page 97.

Rubidium separates in crystals having in general the same habit as those of potassium but showing a tendency to greater elongation and a preponderance of thinner plates and tablets and less crystalline grains and less J-shaped crystals (Fig. 63, page 97).

With cesium the typical form is that of a much-elongated, thin, double wedge with rounded ends. These crystals occur singly, in bristling radiates and irregular clusters and masses. The rhomboidal grains, short, thick tablets, and curved blades of potassium and rubidium are absent; there is also a far greater tendency to form aggregates (Figs. 64 and 65, page 97. By Method IA).

<sup>40</sup> None of the commercial obtainable samples of barbituric acid or nitrobarbituric acid tested by the authors have been found sufficiently free from alkali cations to be satisfactory as reagents for microscopical tests. Only material specially purified in platinum or in silica containers should be used, and even such reagents should be subjected to critical "blank" tests.

It is possible to identify cesium and potassium in the presence of each other and in the presence of sodium, but in mixtures in which rubidium or ammonium is present the nitrobarbituric acid test is not dependable nor is it useful in complicated mixtures containing the heavy metals.

The habit of the ammonium salt (Fig. 62, page 97) is such that its presence in mixture renders this test of no value. The reagent in a hanging drop can be used to identify  $\text{NH}_3$  set free from  $\text{NH}_4$  salts.

Lead forms small rods, singly or in X's, and irregular stars and also thin four-sided plates with rounded angles. These plates may develop into square or rectangular tablets and the rods, more rarely, into elongated prisms. The crystals are strongly birefringent, and as commonly oriented on the object slide exhibit parallel extinction.

Thallium yields tiny, rounded grains and disks, singly, in two's, and in clumps.

$\text{Hg}^{++}$  under the conditions described for the test gives no apparent reaction.

The test is not applicable to salts of antimony and bismuth since it must be made in very dilute, neutral, aqueous solutions. Under these conditions the mineral acid salts of these two elements will be precipitated as antimonyl and bismuthyl salts.

Lithium gives no apparent reaction unless in very concentrated solution and then only after standing for a short time. Masses of very fine needles may form near the periphery of the test drop.

Calcium yields a precipitate of tiny rectangular and square plates or small lath-shaped prisms or rods which are strongly birefringent and appear to be monoclinic. The crystals separate singly, not in aggregates nor in masses nor in laminated groups.

Strontium forms two types of crystals: tiny, irregular, more or less granular or drusy disks or pseudo-spherulites, and, more abundantly, thin plates, usually laminated and much larger than the plates formed by calcium; they are strongly birefringent with colors of the second order. As ordinarily oriented on the slide they exhibit a very small extinction angle.

Barium yields an instantaneous precipitate almost "amorphous" in appearance, which slowly develops into tiny disks and spherulites. These soon sprout and grow into radiates of fine needles whose birefringence is low and requires careful illumination for their resolution. Barium does not form the laminated plates characteristic of strontium.

Magnesium forms very tiny short rods with rounded ends, singly, in X's, and crosses. On standing, thin, slightly elongated plates with more or less rounded ends appear; these plates are probably hexagons with



FIG. 60. Potassium with Nitrobarbituric Acid. 300X.

FIG. 61. Potassium with Nitrobarbituric Acid. 300X.

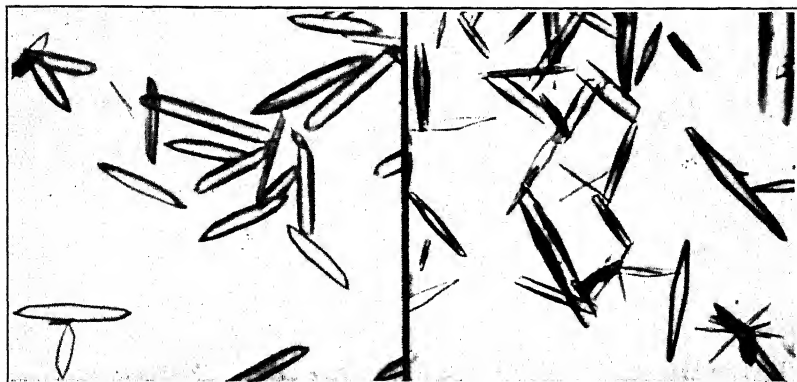


FIG. 62. Ammonium with Nitrobarbituric Acid. 300X.

FIG. 63. Rubidium with Nitrobarbituric Acid. 300X.

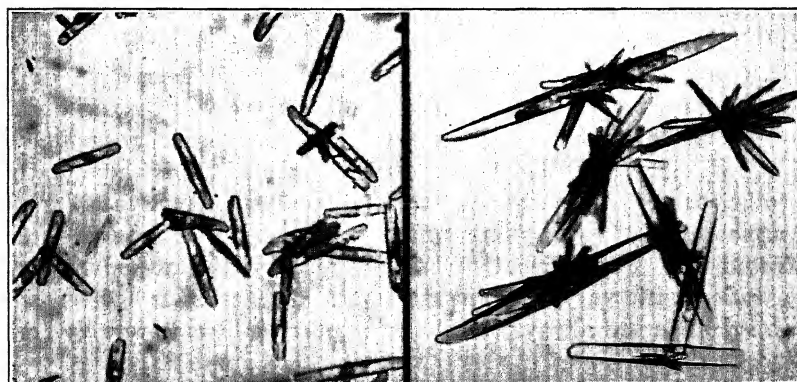


FIG. 64. Cesium with Nitrobarbituric Acid. 300X.

FIG. 65. Cesium with Nitrobarbituric Acid. 300X.

imperfectly developed angles. In certain concentrations the crystals are indistinguishable from those formed by potassium and by ammonium.

Zinc and cadmium yield immediate precipitates consisting of tiny rods and needles, singly and in clusters.

Aluminum, gallium, and indium in moderate concentrations give no immediate reactions but, on standing for a short time, well-formed crystals appear.

Ferric salts form compounds having an appearance similar to the crystals obtained with gallium.

Cobalt, nickel, and manganese yield rods and spindles, singly or in clusters, together with thin plates which are indistinguishable from those formed by the alkaline earths.

$\text{Cu}^{++}$  forms rods and small, thin, lath-shaped plates and prisms, many of which have obliquely truncated ends. They occur singly, in X's, crosses, radiates, and irregular masses. The prisms seen edgewise terminate in thin wedges. A feature which appears to be specific (?) for copper is the occurrence of many curious sinuous rods and dislocated prisms. The crystals are substantially colorless, are strongly birefringent, and exhibit oblique extinction. Under normal conditions, with the exception of the sodium salt, copper nitrobarbiturate grows to larger dimensions in the test drop than any other of the nitrobarbiturates mentioned in this discussion.

Silver in dilute solution closely resembles the reaction given by copper, but the orientation of the plates and prisms is almost invariably such as to exhibit parallel extinction. The silver salt is strongly birefringent with brilliant polarization colors. As with copper, long curved rods occur, but we have failed to obtain preparations which contained the curious sinuous rods which appear to be always present with copper when the reagent is applied as described above.

With gold (chloroauric acid), masses of granular crystals of unidentifiable crystal habit are formed at the periphery of the test drop.

5-Nitrobarbituric acid may be considered as a useful reagent when dealing with simple salts, but is not to be depended upon when mixtures are to be studied. It is essential that the analyst become familiar with the appearance of the crystals which are formed in dilute and in concentrated test drops, since the salts formed by this reagent vary in appearance with varying concentrations. The crystals formed upon an object slide are always small and appear to be colorless by transmitted light.



## GROUP I. SEPARATION METHODS

It sometimes happens that the alkali metals are combined in compounds of such a nature that the direct application of the identity tests are unsatisfactory or misleading, especially when a quantitative "estimate" is desired. Or the alkalis may be present in mixtures with interfering cations or anions. Under such conditions a separation of the alkalis from the alkaline earths, heavy metals, or complex ions is imperative. The following procedures are suggested as means of avoiding possible errors.

**I. The cations present are combined with volatile inorganic anions.**—Several large drops of the aqueous solution are placed in a platinum cup. Solid oxalic acid<sup>41</sup> is added in the proportion of about ten times the weight of the material in solution. The preparation is heated gently until all water has been driven off, great care being exercised to avoid spurting and decrepitation. The temperature is now slowly raised until the oxalic acid sublimes and the heating is continued until sublimation ceases. Usually it is necessary to repeat this treatment at least twice. The temperature is finally raised to a red heat.

The alkalis and the alkaline earths are thus converted into carbonates; magnesium and the heavy metals into oxides.

The mass is extracted with hot water, using as small an amount as possible; the alkali carbonates pass into solution (with part of the lithium). The aqueous solution is evaporated to dryness and portions tested.

If lithium is to be searched for, the residue insoluble in water is dissolved (or extracted) with HCl, the solution evaporated to complete dryness, extracted with isoamyl alcohol, isobutyl alcohol, acetone,<sup>42</sup> diethylene dioxide,<sup>43</sup> or methyl acetate<sup>44</sup> (all these solvents must be anhydrous). Evaporate the extract to dryness and test the residue for lithium (see pages 86–89).

If much material is extracted by the alcohol it may be necessary to precipitate an aqueous solution with  $\text{Ba}(\text{OH})_2$ . Filter, treat the filtrate with HCl; evaporate to dryness; extract the dry residue with isoamyl or isobutyl alcohol or methyl acetate, evaporate the extract, and test the residue for lithium.

<sup>41</sup> Maljaraff: *Mikrochemie* 6, 92 (1928).

<sup>42</sup> Caley: *Ind. Eng. Chem. (Anal. Ed.)* 2, 304 (1930).

<sup>43</sup> Sinka: *Zeit. anal. Chem.* 80, 430 (1930).

<sup>44</sup> Takio Kato: *Jour. Chem. Soc. Japan.* 56, 373 (1935).

II. Separation of the alkalis from materials containing non-volatile inorganic anions (Behrens-Schoorl). — To the aqueous solution add  $\text{BaCl}_2$  or  $\text{Ba}(\text{OH})_2$  in slight excess; filter or centrifuge; to the clear filtrate add  $(\text{NH}_4)_2\text{CO}_3$  to remove the barium; filter or centrifuge. Acidify the filtrate with  $\text{HCl}$ ; evaporate to dryness and ignite to drive off all ammonium salts.

Extract the dry residue as above, warming gently to assist solution of the lithium (and thallium). Evaporate the extract and test the residue for lithium with  $\text{HF}$  and with  $\text{HNa}_2\text{PO}_4$ . Test for thallium with  $\text{KI}$  or  $\text{AuCl}_3$ .

The material insoluble in alcohol is tested for:

$\text{Na}^+$  with  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ .

$\text{K}^+$  with  $\text{H}_2\text{PtCl}_6$  or  $\text{HClO}_4$  ( $\text{NH}_4^+$  must be absent).

$\text{Rb}^+$  with  $\text{H}_2\text{PtCl}_6$  (or  $\text{K}_2\text{PtCl}_6$ ) and also with  $\text{AgCl} + \text{AuCl}_3$ .

$\text{Cs}^+$  with  $\text{H}_2\text{PtCl}_6$  (or  $\text{K}_2\text{PtCl}_6$ ) and also with  $\text{AgCl} + \text{AuCl}_3$  or by Method A, p. 78.

III. Separation of sodium and lithium from potassium, rubidium, and cesium. — Proceed as in II; but, after treatment with  $\text{HCl}$  and ignition to drive off ammonium salts, convert into chloroplatinates and evaporate to dryness. Extract with anhydrous methyl acetate; sodium and lithium chloroplatinates are soluble.

Or convert into perchlorates by treating with perchloric acid. Evaporate to dryness and extract with methyl acetate; sodium and lithium perchlorates are soluble, those of potassium, rubidium, and cesium are insoluble.<sup>45</sup>

IV. Detection of the alkalis in silicates, glass, etc. — The material is crushed in a "diamond" mortar and rubbed into an impalpable powder in an agate mortar. Decomposition is effected by treatments with  $\text{NH}_4\text{F} \cdot \text{HF}$  and  $\text{HCl}(1 : 1)$  or with  $\text{HF}$  and  $\text{HCl}$  at room temperature. Examine the preparation for crystals of  $\text{Na}_2\text{SiF}_6$  and  $\text{NaCl}(\text{KCl}, \text{RbCl}, \text{CsCl})$ .

Treat repeatedly with  $\text{HF}$  (or  $\text{NH}_4\text{F} \cdot \text{HF}$ ) and concentrated  $\text{HCl}$ , heating to expel  $\text{SiF}_4$ . (Treatment with  $\text{HF}$  and  $\text{H}_2\text{SO}_4$  is better.) Fume off the excess of acid, and ignite to expel ammonium salts if  $\text{NH}_4\text{F} \cdot \text{HF}$  has been used.

Extract the residue with warm water. The solution may contain  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$ . Test separate portions for these cations.

If  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Tl}^+$ ,  $\text{Li}^+$  are to be searched for, heat the residue after the expulsion of fluorine and fluorides, as described in I and II, according to whether  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  has been used.

<sup>45</sup> Takio Kato: *op. cit.*

## CHAPTER IV

### THE DETECTION OF THE ELEMENTS OF GROUP II

Be; Ca, Sr, Ba; Mg, Zn, Cd; Hg

The element beryllium, heading Group II, like all the other elements of lowest atomic weight in each of the first seven vertical groups of the Periodic System, is transitional in its chemical properties. In most of its compounds beryllium resembles magnesium and zinc, but in others the resemblance to aluminum is more marked than to magnesium.

Because of its marked transitional character beryllium can give rise to crystalline compounds which may make their appearance in testing for the presence of Group I, Group II, or Group III. Its salts are colorless and lack characteristic features; hence the microscopical detection of beryllium in mixtures is always difficult, and unsatisfactory.

Like the alkalis beryllium forms a crystalline chloroplatinate. (See Potassium, page 67.)

Unlike magnesium, zinc, and cadmium, beryllium does not readily form a triple acetate with sodium and uranyl; even if these cations and anions are present in the proper concentration to produce the triple salt, it will not separate until the preparation has evaporated to dryness.

Salts of beryllium are precipitated by NaOH and KOH,  $\text{Be}(\text{OH})_2$  being formed. This compound is soluble in an excess of alkali because of the formation of a berylate  $\text{Be}(\text{ONa})_2$  or  $\text{Be}(\text{OK})_2$ . In this respect beryllium resembles zinc (cadmium), and the aluminum group; but unlike aluminum, beryllium hydroxide is soluble in  $\text{NH}_4\text{OH}$ . Beryllium does not form "alums." Most salts of beryllium are hydrolyzed if their aqueous solutions are boiled.

In most of its compounds beryllium bears a closer resemblance to magnesium than to aluminum, but does not form sulphates which are isomorphous with those of magnesium.

In dilute solutions of beryllium salts, oxalic acid produces no precipitate (distinction from the scandium group of Group III), but in concentrated solutions beryllium forms a readily crystallizable oxalate of sufficiently low solubility to separate in a test drop; in this it resembles calcium, strontium, and barium. Its relation to the primary subgroup of Group II is further shown by the low solubilities of its carbonate and its phosphate (relation to lithium), but its very soluble

sulphate, chromate, ferrocyanide, and iodate set it apart from the alkaline earths and rare earths.

In the group, calcium, strontium, and barium, there is but one salt of these elements, the fluoride, which links this group with the group of the alkalis. Like the normal fluorides of lithium, sodium, potassium, rubidium, and cesium, the normal fluorides of calcium, strontium, and barium are isotropic and crystallize in cubes and octahedra, and they may thus be confused with the fluorides of the alkalis when HF is employed as a reagent.

Although the alkaline earths are very closely related one to another in their general properties, the differences in the solubilities of their typical salts and the differences in the appearances of these salts on the object slide enable the analyst to differentiate readily between them. There is also little danger of confusing them with other members of Group II, though it is well to bear in mind that if the ions  $\text{Ag}^+$ ,  $\text{Hg}^+$ , or  $\text{Pb}^{++}$  are present, crystalline compounds may be obtained when testing for the alkaline earths.

In the presence of phosphates, arsenates, vanadates, molybdates, and tungstates the identification of the alkaline earths may prove difficult unless separation methods are employed before specific tests are applied.

The element magnesium falls in a microanalytical group by itself, save for its behavior with  $\text{Na}^+$  and  $\text{UO}_2^{++}$  acetates. Unlike its near relatives zinc and cadmium, it does not form a difficultly soluble double thiocyanate with mercury, while its very soluble sulphate, chromate, ferrocyanide, oxalate, and tartrate set it apart from the alkaline earths and its soluble iodide differentiates it from mercury. Its hydroxide is not soluble in NaOH or KOH.

Mercury also must be set apart by itself and made the object of special tests. Save when in the mercurous state, this element shows little in common with the other elements in Group II so far as microscopical qualitative analysis is concerned.

Cadmium chloride forms complex crystalline salts with the chlorides of many elements. Ferrari has advanced the hypothesis that many of these compounds should be regarded as "cadmates" (or chlorocadmates) — *e.g.*,  $\text{Cs}_2\text{Cd}(\text{CdCl}_6)$ ,  $\text{BaCd}_2\text{Cl}_6 \cdot 5 \text{H}_2\text{O}$  (see also footnote, page 80).

## DETECTION OF CALCIUM, STRONTIUM, BARIUM

### A. By Means of Ammonium Carbonate — $(\text{NH}_4)_2\text{CO}_3$ .

*Compounds Formed* —  $\text{CaCO}_3$

$\text{SrCO}_3$

$\text{BaCO}_3$ .

To a moderately concentrated solution of the material to be tested, neutral if possible, or at the most only very slightly acid, add one or more fragments of "ammonium carbonate"<sup>1</sup> (Method II, page 33). *Warm gently*, but avoid boiling. An excess of the reagent and avoiding boiling are essential since otherwise the reaction is a reversible one. The reaction is slow; the precipitate first formed is "amorphous" and only becomes crystalline on standing (Fig. 74, page 109). Of the three alkaline-earth carbonates formed in this manner, that of barium is least soluble, and that of calcium most soluble. All three are dimorphic; the crystals are either hexagonal or orthorhombic, according to conditions. If the temperature has not been too high, hexagonal forms should be obtained in the test.

Calcium gives tiny disks and well-defined rhombohedra; strontium gives spherulites and dumb-bell aggregates of tiny needles; while barium maintains an "amorphous" form for a relatively long period and only partially changes to minute needles, spider-like aggregates, and tiny spherulites; the latter sometimes develop into spindles and dumb-bell masses. Strontium and barium carbonates are generally indistinguishable. All three carbonates are strongly birefringent. It is obvious that only in the case of calcium are characteristic crystals obtained.

$(\text{NH}_4)_2\text{CO}_3$  gives flocculent or granular precipitates with a large number of elements; hence this test is of little value in complex mixtures, but since the alkaline earth carbonates generally cling tightly to the object slide, precipitation with  $(\text{NH}_4)_2\text{CO}_3$  may be a valuable means for group separations, for decantation is easily performed and the precipitate clinging to the slide may then be washed, and dissolved in acetic acid for the application of identity tests.

The reaction of  $(\text{NH}_4)_2\text{CO}_3$  with lithium has already been described on page 88.

$\text{HNaCO}_3$  and  $\text{HKCO}_3$  give reactions similar to  $(\text{NH}_4)_2\text{CO}_3$ , but when in large excess and heated at or near the boiling point double salts are formed, which in the case of calcium afford characteristic reactions. The formation of the salt  $\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 5\text{H}_2\text{O}$  has been suggested for the detection of calcium in simple mixtures, in plant juices, and in vegetable and animal tissues.

$\text{HNaCO}_3$  in excess yields a characteristic test for Zinc. (See page 145.)

$\text{Na}_2\text{CO}_3$  produces "amorphous" precipitates that in the case of

<sup>1</sup> This reagent as ordinarily encountered consists of a mixture of carbonate, bicarbonate, and carbamate. Carbamates of the alkaline earths are soluble, but unstable and converted into carbonates on heating.

strontium and barium retain their non-crystalline appearance on standing. Calcium carbonate slowly becomes crystalline if neither strontium nor barium is present.<sup>2</sup>

Hexagonal  $\text{CaCO}_3$  (calcite) is isomorphous with hexagonal  $\text{MgCO}_3$ ,  $\text{FeCO}_3$ ,  $\text{MnCO}_3$ ,  $\text{CoCO}_3$ ,  $\text{ZnCO}_3$ , and the solid solution of these carbonates with calcium carbonate.  $\text{CaCO}_3$  is also theoretically isomorphous with hexagonal  $\text{NaNO}_3$ .<sup>3</sup>

Orthorhombic  $\text{CaCO}_3$  (aragonite) is isomorphous with orthorhombic  $\text{SrCO}_3$ ,  $\text{BaCO}_3$ , and  $\text{PbCO}_3$  and also with orthorhombic  $\text{KNO}_3$ .

Hexagonal  $\text{CaCO}_3$ —calcite—is the stable form, and orthorhombic  $\text{CaCO}_3$ —aragonite—the metastable, but if even only very little  $\text{SrCO}_3$  or  $\text{PbCO}_3$  is present aragonite is stabilized (Mellor).<sup>4</sup>

In view of these isomorphous series, it is evident that the alkaline earth carbonates will carry down with them other elements which may complicate an analysis.

It is obvious that ammonium carbonate has little in its favor as an identity test. Nevertheless it has been placed first ("A") in the Group because the reaction product is of great value as a starting point in the routine qualitative analysis of material of wholly unknown composition. Any precipitate obtained can be separated and converted into salts which may be readily and rapidly subjected to specific reagents. Moreover the presence or the absence of a precipitate with ammonium carbonate yields information at once relative to a fairly large number of cations and may thus materially shorten the time required for an analysis.

### Experiments.

(a) Test in turn a calcium, a strontium, and a barium salt, with  $(\text{NH}_4)_2\text{CO}_3$ , using very dilute solutions.

(b) Decant the mother liquor from the precipitated carbonates, and cover the residue with dilute  $\text{H}_2\text{SO}_4$ . Note the conversion to sulphates.

<sup>2</sup> Molisch: *Ber. d. bot. Ges.* 34, 288, 357 (1916), suggests  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$  as exceptionally sensitive reagents for the demonstration of  $\text{Ca}^{++}$  in plant tissues, no matter in what form the  $\text{Ca}^{++}$  may be combined. If calcium carbonate is present in the tissues it suffices to add concentrated  $\text{KOH}$ ; after a short time crystals of  $2\text{CaCO}_3 \cdot \text{K}_2\text{CO}_3$  appear as hexagonal plates. As a test for calcium, concentrated  $\text{KOH}$  saturated with  $\text{K}_2\text{CO}_3$  will detect  $\text{Ca}$  when combined as phosphate, oxalate, etc., in plant cells.

<sup>3</sup>  $\text{CaCO}_3$  exists in three crystal phases; see Johnston, Merwin and Williamson: *Amer. Jour. Sci.* 191, 473 (1930).

<sup>4</sup> It is sometimes desirable to be able to determine whether poorly developed crystals are calcite or aragonite and observations as to their uniaxial or biaxial character are uncertain. In some cases their behavior when illuminated with ultra-violet light may prove an aid—aragonite fluoresces, calcite does not. Or observations on refractive indices may be of value: in calcite  $\omega = 1.658+$ ,  $\epsilon = 1.486+$ ; but in aragonite  $\alpha = 1.530$ ,  $\beta = 1.681$ ,  $\gamma = 1.685$ .



FIG. 66. Barium with Iodic Acid.  
100X.

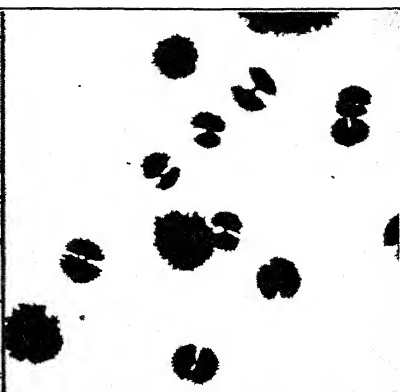


FIG. 67. Strontium with Iodic Acid.  
100X.

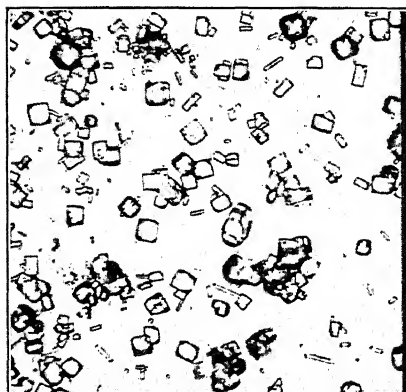


FIG. 68. Calcium with Potassium  
Ferrocyanide. 800X.

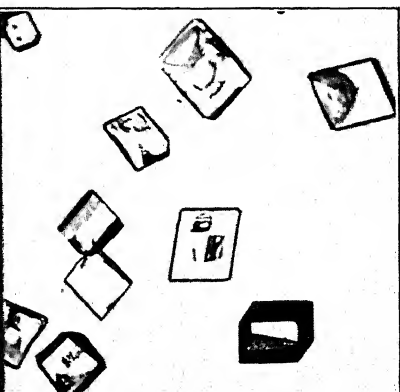


FIG. 69. Barium with Potassium  
Ferrocyanide. 70X.

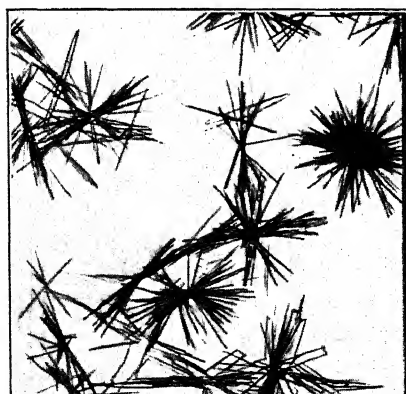


FIG. 70. Calcium with Sulphuric  
Acid. 100X.

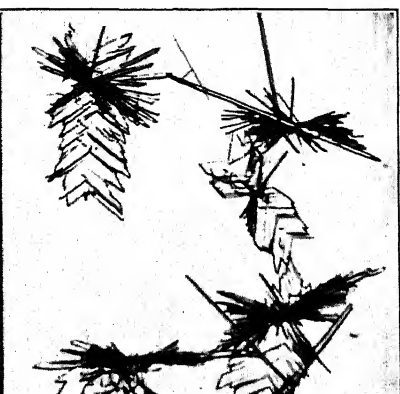


FIG. 71. Calcium with Sulphuric  
Acid. 100X.

**B. By Means of Dilute Sulphuric Acid —  $\text{H}_2\text{SO}_4$ .<sup>5</sup>**

*Compounds Formed* —  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .



Apply the reagent by Method I, page 31, to a cold, neutral (or very slightly acid), moderately concentrated test drop.

Free  $\text{HCl}$  or  $\text{HNO}_3$  retard the separation of the crystals of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; but, if the concentration of  $\text{Ca}^{++}$  is high, this retardation may be a distinct gain, for more characteristic crystals are obtained.

The first crystals usually appear at the periphery of the test drop nearest the reagent. They are long, slender, colorless needles, exhibiting oblique extinction (monoclinic) (Fig. 70, page 105). These needles first terminate in very slender points, but later as they develop into long, narrow, thin, monoclinic prisms the ends become irregularly obliquely truncated (the acute angle is approximately  $66^\circ$ , a feature that is very characteristic of this salt). Needles and prisms occur singly, in sheaves, rosettes, X's, and irregular fragments. With time the prisms broaden into masses of thin plates piled over one another like scales or shingles. These masses are built up of twins or fourlings. This change from acicular crystals to plates is specific for  $\text{Ca}^{++}$  (Fig. 71, page 105).

$\text{Bi}^{+++}$  and  $\text{Hg}^+$  may under certain conditions yield sheaves and rosettes of acicular crystals but in neither case do the needles develop into long thin prisms with obliquely truncated ends, and never do they give plates in twins and fourlings like  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

If no crystals of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  appear at first, set the preparation aside, examining it from time to time. This procedure is safer than heating to hasten evaporation or the addition of alcohol to reduce the solubility of the calcium sulphate. Moreover, if heated too high,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  passes over into  $\text{CaSO}_4$ ,<sup>6</sup> thus introducing a crystallographic complication.

In solutions of concentrations such that the calcium salt is incompletely dissociated (that is, that  $\text{Ca}^{++}$  is in whole or in part present

<sup>5</sup> For a discussion of the use of sulphates as reagents instead of  $\text{H}_2\text{SO}_4$  and the appearance of the crystalline precipitates obtainable, see Rosenthaler: *Mikrochemie* 14, 268 (1934).

In most cases  $\text{H}_2\text{SO}_4$  is the most satisfactory reagent for the detection of the calcium group and should therefore have been given the designation "A." It is, however, frequently better to test first with  $(\text{NH}_4)_2\text{CO}_3$  or with  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and apply to the precipitates thus obtained the more specific test with  $\text{H}_2\text{SO}_4$ .

<sup>6</sup> See Mellor: *Comprehensive Treat. Inorgan. and Theoret. Chem.*, Vol. III, p. 779.



in a complex) the separation of the salt  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  is more or less inhibited. Boron complexes are especially detrimental (Behrens). Boiling the "unknown" with concentrated  $\text{HNO}_3$  will usually destroy the complex; but under these conditions all excess of  $\text{HNO}_3$  must be driven off since  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  is soluble in this acid.  $\text{HNO}_3$  appears to give better results than treatment with  $\text{HCl}$ . Moreover, it has been shown that  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  is not readily formed in the presence of much  $\text{CaCl}_2$ .

Staples<sup>7</sup> has called attention to the fact that when much  $\text{Na}^+$  is present a precipitate of  $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$  may be obtained in the form of orthorhombic pseudo-hexagonal prisms, either alone or with  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ . These prisms exhibit parallel extinction when lying on a prism face and a birefringence higher than gypsum. In crystals of the hemihydrate the slow ray is lengthwise the crystal, but in gypsum it is the fast ray which is lengthwise. The hemihydrate is also obtained [Gaubert: *Compt. rend.* 197, 72 (1933)] in pseudo-rhombohedral when a nitric acid solution of gypsum is concentrated by boiling.

Before deciding that calcium is absent, it is wise to test for the presence of  $\text{NH}_4$  (i.e.,  $\text{NH}_3$ ). Under certain conditions of concentration, calcium sulphate is soluble in ammonium sulphate because of the formation of the double salt  $\text{CaSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ . This double salt is decomposed by an excess of water, with reprecipitation of  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ , but no dependence should be placed upon this probable reprecipitation in microscopical qualitative analysis.

Most salts of the trivalent metals interfere more or less seriously with the sulphate test for calcium. Under these conditions, it is best to precipitate the alkaline earths with ammonium oxalate in neutral concentrated solution, separate, and wash (once) the precipitate by means of the centrifuge. Then recrystallize the precipitate from  $\text{H}_2\text{SO}_4$ .

Strontium yields a granular crystalline precipitate. Sometimes, if viewed immediately after the inflow of the reagent, sheaves and masses of very tiny acicular crystals of  $\text{SrSO}_4$  are seen, but these rapidly disintegrate into a granular deposit in which even a high power fails to reveal any distinctive features. Strontium sulphate is readily converted into strontium carbonate on boiling with ammonium carbonate. Addition of nitric acid to the cooled solution dissolves the precipitated strontium carbonate. The barium sulphate which may be in the mixture remains practically unaffected.

Because of its very low solubility and precipitation at room temperatures,  $\text{BaSO}_4$  usually separates in so finely divided a condition as to appear to be amorphous under the magnifications applicable to uncovered drops in microscopical qualitative analysis. Rarely the

<sup>7</sup> *Amer. Mineralogist* 21, 625 (1936).

precipitate obtained may consist of tiny, more or less rectangular grains. Digestion of the "amorphous" precipitate with HCl will usually yield small, well-defined tabular grains.

Lead also forms a sulphate,  $\text{PbSO}_4$ , of very low solubility, and is generally precipitated at once in a finely dispersed condition not distinguishable from  $\text{BaSO}_4$ . In a short time, however, this fine precipitate becomes granular and is then indistinguishable from  $\text{SrSO}_4$ ; still later crystallites and skeleton crystals may appear, the most characteristic form being X's with peculiar curved arms, and these in turn may develop into rhombic plates. Very rarely, the addition of  $\text{H}_2\text{SO}_4$  causes the separation of well-formed orthorhombic prisms.  $\text{PbSO}_4$  is soluble in NaOH and in  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  solutions, but the sulphates of the alkaline earths are not appreciably soluble in these reagents. When in doubt, decant, wash the precipitate, and add a fragment of KI. Allow to stand a few minutes. If lead is present, yellow hexagons and yellow micaceous scales will be formed. (See page 203.) If lead is present together with the calcium group, the precipitate will probably be a mixed sulphate from which the lead can be separated only in part by digestion with sodium acetate; but sufficient lead passes into solution to permit its identification.

The sulphates of  $\text{Hg}^+$  and  $\text{Ag}^+$  (see  $\text{SO}_4^{--}$ , page 349) are only slightly soluble in water and therefore will separate if present, but since they form moderately large crystals or aggregates they cannot be mistaken for the alkaline earths. The same is true of  $\text{Tl}^+$ .  $\text{Bi}^{+++}$  and  $\text{Sb}^{+++}$  may be precipitated as white basic salts.

A saturated solution of  $\text{CaSO}_4$  gives no precipitate with salts of  $\text{Ca}^{++}$ , but causes a slow separation of  $\text{SrSO}_4$  and an immediate separation of  $\text{BaSO}_4$ .

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is converted into  $\text{CaCO}_3$  by heating with  $(\text{NH}_4)_2\text{CO}_3$  solution, and if heated with an alkali tartrate  $\text{CaC}_4\text{H}_4\text{O}_6$  is formed.

Calcium selenate,  $\text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$ , is isomorphous with  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , but is more soluble than the latter and therefore unsuited for the detection of  $\text{Ca}^{++}$ .

It has been implied above that many compounds when in concentrated solutions materially increase the solubility of calcium sulphate. If the solubility of calcium sulphate in water be taken as unity, the ratio increase in solubility in round numbers at  $20^\circ$ – $25^\circ$  may be expressed thus:<sup>8</sup>

$\text{H}_2\text{SO}_4$ .....	10×	$\text{MgCl}_2$ .....	26×	$(\text{NH}_4)_2\text{SO}_4$ .....	8×
$\text{H}_3\text{PO}_4$ .....	20×	$\text{NH}_4\text{NO}_3$ .....	18×	Alkali sulphates...	4×
$\text{NH}_4\text{Cl}$ .....	20+×	$\text{CaNO}_3$ .....	5×	$\text{MgSO}_4$ .....	7×
Alkali halides...	17–×	$\text{Mg}(\text{NO}_3)_2$ .....	26×	$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ .....	4×
$\text{CaCl}_2$ .....	5×				

<sup>8</sup> Calculated from data in Comey: *Dictionary of Solubilities*; Seidell: *Solubilities of Inorganic and Organic Compounds*.

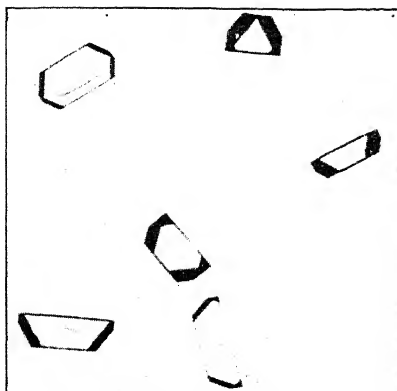


FIG. 72. Calcium with Sodium Tartrate. 100X.



FIG. 73. Calcium with Arsenic Acid. 50X.

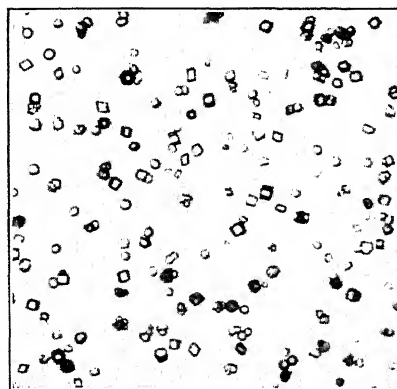


FIG. 74. Calcium with Ammonium Carbonate. 500X.

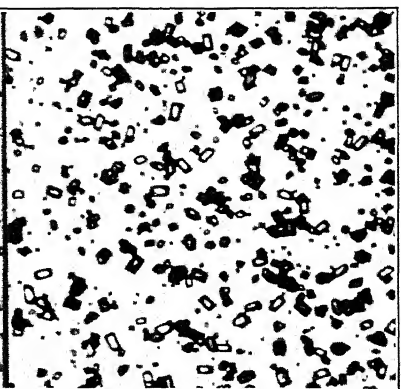


FIG. 75. Barium with Potassium Chromate. 500X.



FIG. 76. Magnesium with Disodium Phosphate and Ammonium Hydroxide. 50X.



FIG. 77. Magnesium with Disodium Phosphate and Ammonium Hydroxide. 100X.

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is readily soluble in  $\text{HCl}$  at room temperature;  $\text{SrSO}_4$  is only slightly so; while  $\text{BaSO}_4$  is practically insoluble. The granular precipitate of  $\text{SrSO}_4$  is soluble in boiling  $\text{HCl}$  from which it separates on cooling in sheaves of acicular crystals, long thin prisms, short rods, and square and rectangular plates.  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  separates from  $\text{HCl}$  solutions without change of habit. Although the crystals of  $\text{SrSO}_4$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  obtained by recrystallization from  $\text{HCl}$  usually differ in appearance, they may appear sufficiently alike to lead to doubt in the mind of the analyst. Recrystallization from  $\text{HCl}$  or  $\text{HNO}_3$  is of very doubtful value as a means of distinguishing between  $\text{Ca}^{++}$  and  $\text{Sr}^{++}$ , but the varying solubilities of the sulphate compounds afford a means of separating the alkaline earths.

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is 2000 times, and  $\text{SrSO}_4$  40 times as soluble as  $\text{BaSO}_4$  in water at room temperatures.<sup>9</sup>

### C. By Heating the Precipitated Sulphates with Concentrated Sulphuric Acid.

*Calcium is absent in the test drop* as ascertained by the method discussed above (B). The drop containing the precipitate is evaporated to dryness so as to cause the amorphous sulphates to cling to the glass. Carefully cover the dry precipitate with water; then warm gently, decant, and reject the wash water. Scrape the insoluble material into a compact mass at the corner of the slide; cover the mass with a drop of concentrated sulphuric acid. Heat until copious white fumes of  $\text{SO}_3$  are evolved, being careful to hold the object slide tipped and to apply the heat of the micro flame above the drop of acid in order to prevent the hot  $\text{H}_2\text{SO}_4$  from creeping over the slide. As soon as it is evident that the bulk (or all) of the precipitate has passed into solution, remove from the flame, tip the slide so that all the acid collects at the corner of the slide, and touch this drop of hot acid to the surface of a clean slide; a small, moderately rounded, clear drop should be thus obtained.  $\text{SrSO}_4$  or  $\text{BaSO}_4$  has passed into solution owing to the formation of acid sulphates  $\text{Sr}(\text{HSO}_4)_2$ ,  $\text{Ba}(\text{HSO}_4)_2$ . These acid sulphates are readily decomposed by water with the reprecipitation of the normal sulphates. If this decomposition is slow, the normal sulphates are given an opportunity to crystallize. Reprecipitation is effected by breathing gently upon the acid drop, once or twice, and allowing the preparation to stand at room temperature. In a few seconds crystals of the normal sulphates appear, at first about the circumference of the drop and later throughout its entire volume.

<sup>9</sup> Schoorl (quoting deKoninck): *Beiträge z. Mikrochem. Anal.* (Weisbaden, 1909), p. 113.

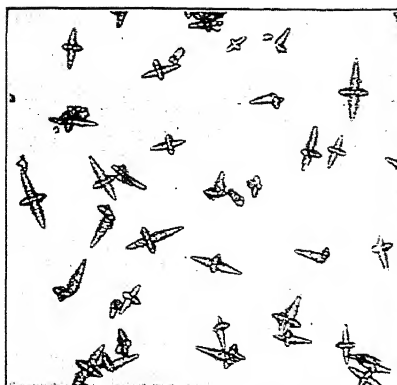


FIG. 78. Strontium Sulphate Recrystallized from Conc. Sulphuric Acid. 200 $\times$ .

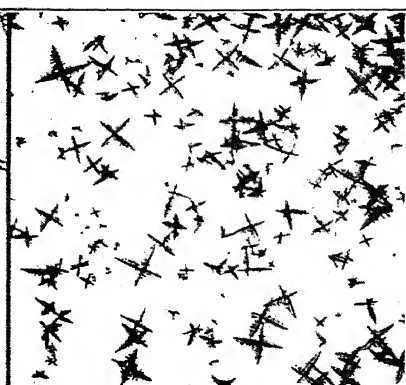


FIG. 79. Barium Sulphate Recrystallized from Conc. Sulphuric Acid. 200 $\times$ .

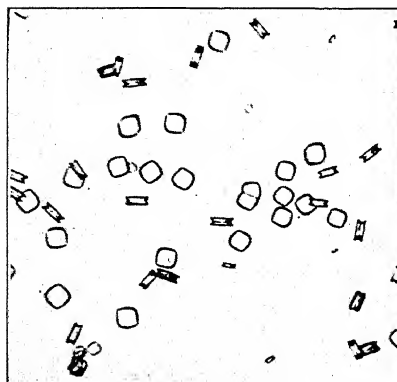


FIG. 80. Calcium with Oxalic Acid. 400 $\times$ .

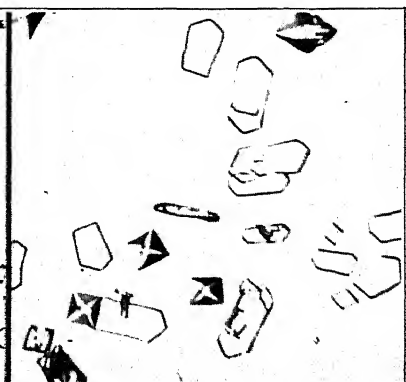


FIG. 81. Strontium with Oxalic Acid. 250 $\times$ .

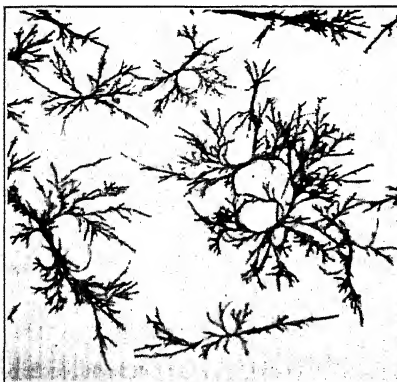


FIG. 82. Barium with Oxalic Acid. 100 $\times$ .

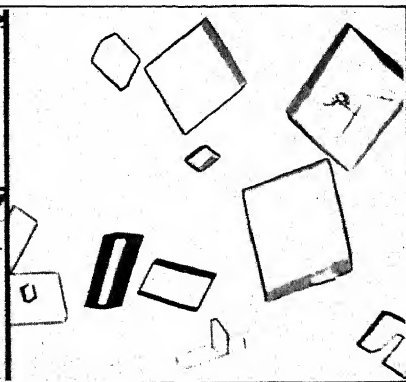


FIG. 83. Beryllium with Potassium Oxalate. 100 $\times$ .

When recrystallized thus,  $\text{SrSO}_4$  separates in the form of irregular granules, fusiform bodies, rhombic plates, and, most characteristic of all, spindle-shaped crystals swelling at the middle of their length so as to give the appearance of slender crosses with tapering arms; both of the cross-arms being very short, the crystals may appear dagger-shaped (Fig. 78, page 111).

If members of Group I are present in large amount in the sample to be tested and the precipitated sulphates have not been well washed, the recrystallized strontium sulphate may separate in the form of rounded bodies oval in outline having none of the characteristics shown in Fig. 78.

$\text{BaSO}_4$  separates in very different crystal forms. Instead of the slender fusiform crystals and crosses with two short cross-arms, X-shaped skeletons with more or less feathery arms appear; usually two of the arms are much longer than the other two, and, since the shorter are always on the same side, the crystals have somewhat the appearance of a distant view of a flying bird. These X's grow quite large and are constant and peculiar to  $\text{Ba}^{++}$ . When the X's are small and are cross-like, the arms are nearly symmetrical but cannot be confused with the crosses of fusiform crystals of  $\text{SrSO}_4$  (Fig. 79, page 111). The preparation containing the acid sulphates should not be allowed to stand for any length of time in a humid atmosphere, or water may be absorbed and  $\text{Sr}(\text{HSO}_4)_2 \cdot \text{H}_2\text{O}$  and  $\text{Ba}(\text{HSO}_4)_2 \cdot 2 \text{H}_2\text{O}$  may be formed.

Mixtures of  $\text{SrSO}_4$  and  $\text{BaSO}_4$  may occasionally yield typical crystals of both  $\text{SrSO}_4$  and  $\text{BaSO}_4$ , but usually the mixed, reprecipitated sulphate possesses the characteristics of neither element.

$\text{PbSO}_4$ , when dissolved in concentrated  $\text{H}_2\text{SO}_4$  and reprecipitated as above described, separates first in forms closely simulating  $\text{SrSO}_4$  (Fig. 123, page 183), and later the skeleton crystals may become feathery and resemble  $\text{BaSO}_4$ . If a fragment of KI is added,  $\text{PbI}_2$  is formed. See Pb, page 203.)

In order to obtain characteristic crystals of  $\text{SrSO}_4$ ,  $\text{BaSO}_4$ , or  $\text{PbSO}_4$ , the  $\text{H}_2\text{SO}_4$  used must be pure. Acid which has stood in small reagent bottles for a long time usually dissolves sufficient material from the glass to prevent the formation of characteristic crystals.

$\text{SrSO}_4$  can be recrystallized by boiling with strong  $\text{HCl}$ , in which  $\text{BaSO}_4$  is practically insoluble. On cooling there will separate, square and rectangular plates, long thin prisms, sheaves of acicular crystals, and short rods. The crystals obtained from  $\text{HCl}$  solutions are not as characteristic as those from hot concentrated  $\text{H}_2\text{SO}_4$ , and are valuable only as a means of distinguishing between strontium and barium; but lead must be absent.

*Calcium is present:*  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  can be recrystallized from hot concentrated  $\text{H}_2\text{SO}_4$  as described above, but the reprecipitated salts  $\text{CaSO}_4$ , or  $\text{Ca}(\text{HSO}_4)_2$  or a mixture of the two are not sufficiently characteristic in appearance to serve in microscopical qualitative analysis. Usually somewhat oval granular plates first appear; these in a short time "sprout" at the ends and grow into tufts of tiny needles or curving dendritic masses.

Calcium seriously interferes with the detection of strontium and barium if the recrystallization method is employed. Trivalent elements also interfere with the formation of typical crystals of the acid sulphates of Sr and of Ba and should therefore be removed by thorough washing of the precipitated sulphates before treatment with hot concentrated  $\text{H}_2\text{SO}_4$ .

Before treating the precipitated sulphates with  $\text{H}_2\text{SO}_4$ , the  $\text{CaSO}_4$  should be removed by one of the following methods:

1. Extract repeatedly with hot distilled water.
2. Extract the sulphates with dilute  $\text{HNO}_3$  (0.1 N) at room temperature.  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is readily soluble;  $\text{SrSO}_4$  only slightly soluble;  $\text{BaSO}_4$  is almost insoluble.
3. Boil the sulphates with a solution of  $\text{NaKC}_4\text{H}_4\text{O}_6$ . Calcium sulphate alone is converted into tartrate.  $\text{CaC}_4\text{H}_4\text{O}_6$  is readily soluble in dilute  $\text{HCl}$ . Decant and wash the precipitate.
4. Boil the sulphates with a concentrated solution of  $(\text{NH}_4)_2\text{CO}_3$ . Calcium and strontium are converted into carbonates but  $\text{BaSO}_4$  remains unchanged.
5. Boil the sulphates with  $\text{HCl}$ . (See Calcium, page 110.)
6. *Lead is present:* This is ascertained by testing for lead in the original material or by adding  $\text{KI}$  to a portion of the sulphates.  $\text{PbI}_2$  is formed.

a. Extract the  $\text{PbSO}_4$  by heating with a concentrated solution of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  in which  $\text{PbSO}_4$  is soluble.

b. Extract with a moderately concentrated solution of  $\text{NaOH}$ , in which  $\text{PbSO}_4$  is soluble; but unless the concentrations are just right a hydrated oxide of lead may be formed which does not entirely pass into solution.

7. *After removing  $\text{Ca}^{++}$  and  $\text{Sr}^{++}$ , recrystallize the residue of  $\text{BaSO}_4$  by heating with  $\text{H}_2\text{SO}_4$ .*

### Experiments.

(a) Precipitate  $\text{CaSO}_4$  by means of dilute  $\text{H}_2\text{SO}_4$ , from a salt of calcium in neutral solution.

(b) Try the effect of precipitating in the presence of free HCl; then in the presence of free  $\text{HNO}_3$ .

(c) Precipitate with dilute  $\text{H}_2\text{SO}_4$ , then heat, adding more acid if necessary, until white fumes are given off; cool, breathe on the preparation, and examine.

(d) Try testing for a trace of Ca in the presence of a large quantity of salts of the elements of Group I. A retardation of the reaction results.

(e) Try effect of a solution of  $(\text{NH}_4)_2\text{CO}_3$  on crystals of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

(f) To a drop of moderately dilute solution of  $\text{SrCl}_2$ , add dilute  $\text{H}_2\text{SO}_4$ , and examine at once.

(g) Recrystallize  $\text{SrSO}_4$  from  $\text{H}_2\text{SO}_4$  and from HCl.

(h) Make a mixture of Ca and Sr salts and add  $\text{H}_2\text{SO}_4$ . Recrystallize the product from  $\text{H}_2\text{SO}_4$  without having removed the Ca. In another portion remove the Ca by extracting with boiling water and then recrystallize the residue.

(i) Precipitate  $\text{BaSO}_4$  by means of dilute  $\text{H}_2\text{SO}_4$ , from a very dilute solution of a barium salt.

(j) Make a mixture of salts of Ca and Ba; recrystallize at once without removing the Ca. From another portion remove the Ca with hot water and recrystallize the residue.

(k) Try a mixture of Sr and Ba. Remove the Sr by treating with HCl and recrystallize the residue.

(l) Try a mixture of Ca, Sr, and Ba, recrystallizing at once, then removing in turn the Ca with hot water and the Sr with HCl.

(m) After having tried the other reactions for Ba, fuse some  $\text{BaSO}_4$  with  $\text{K}_2\text{CO}_3$  and proceed as directed above.

#### D. By Means of Oxalic Acid — $\text{H}_2(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ .

*Compounds Formed* —  $\text{Ca}(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$

$\text{Sr}(\text{C}_2\text{O}_4) \cdot n\text{H}_2\text{O}$

$\text{Ba}(\text{C}_2\text{O}_4) \cdot n\text{H}_2\text{O}$ .

Apply the reagent, at room temperature, by Method I, page 31, to a neutral solution or to one slightly acidulated with acetic acid.

Under these conditions, the calcium salt obtained will be  $\text{Ca}(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$  in the form of tiny, highly refractive, strongly birefringent tetragonal octahedra, rhombs, drusy crosses, rectangular plates, or tablets which are almost square (Fig. 80, page 111). From hot solutions or those containing a small amount of free mineral acid, the monoclinic salt  $\text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$  may separate; this monohydrated oxalate has little value in microscopical qualitative analysis since its habit is such as to render very difficult its differentiation from the oxalates of many other elements.

$\text{Ca}(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$  is only slightly soluble in solutions containing acetic acid, alkali acetates, or ammonium hydroxide, but is very soluble in dilute mineral acids. Hence before testing for the alkaline earths with oxalic acid, it is wise to add sodium or ammonium acetate to the test drop. A trace of free  $\text{HNO}_3$  is sometimes desirable, however, when



only  $\text{Ca}^{++}$  salts are present and their concentration high, for the separation of  $\text{Ca}(\text{C}_2\text{O}_4) \cdot 3 \text{H}_2\text{O}$  is retarded, and larger and more easily recognized crystals are obtained. The separation of crystals of  $\text{Ca}(\text{C}_2\text{O}_4) \cdot 3 \text{H}_2\text{O}$  may be materially retarded in the presence of a number of salts, prominent among which are alkali chlorides and borates. Tartrates and citrates may completely inhibit the test.<sup>10</sup>

The oxalate test should always be confirmed by the sulphate test. The mother liquor is decanted from the precipitated oxalates, or recourse may be had to filtration or to the centrifuge. Wash at least once with distilled water. Scrape together the precipitate and cover with a moderate-sized drop of dilute  $\text{H}_2\text{SO}_4$ ; calcium oxalate will be dissolved and in a few minutes characteristic crystals of  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  will be obtained if calcium is present.

Strontium gives with oxalic acid  $\text{SrC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ , in either tetragonal or monoclinic crystals, depending upon temperature conditions. At room temperature the tetragonal form may be expected. This salt separates in "octahedra," and in symmetrical crosses with pointed arms bounded by curves; the latter are skeleton crystals and are forms rarely obtained with calcium oxalate. On long standing, six-sided plates or square and rectangular, short, stout bipyramidal prisms appear (Fig. 81, page 111). Usually the oxalate crystals formed by strontium are not readily distinguished from the corresponding oxalates of calcium save that they are apt to be larger and better developed. In mixtures the two oxalates are indistinguishable; recourse may then be had to the  $\text{H}_2\text{SO}_4$  treatment described above.

Barium also forms with  $\text{H}_2\text{C}_2\text{O}_4$  several oxalates  $\text{BaC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ . At room temperature the crystals separating are very different from those obtained with calcium or strontium; large branching aggregates in fibrous bundles or sheaf-like masses of fibrous drusy dendrites are obtained (Fig. 82, page 111). Not infrequently small monoclinic prisms are also formed, but the latter are in no way characteristic.  $\text{BaC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$  is soluble in  $\text{HC}_2\text{H}_3\text{O}_2$ , readily so if heated, and is so soluble in  $\text{HNO}_3$  that a bare trace of this acid will prevent the separation of  $\text{BaC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$  in the test drop. If calcium or strontium is also present, the characteristic branching aggregates of barium oxalate will not be obtained. Advantage may then be taken of the much greater solubility of the barium salt in nitric acid. To the test drop, nitric acid is very cautiously added in an amount just sufficient to make the solution faintly acid. Usually what may be called a bare trace of acid is all that is required; more than this must not be added, since the oxalates of all three alkaline earths are readily soluble in dilute

<sup>10</sup> Evers: *Analyst* 56, 293 (1931).

hydrochloric and in dilute nitric acids. To the acidified drop, the oxalic acid reagent is added. The preparation is allowed to stand for a short time. The barium in solution is then decanted from the precipitated calcium and strontium, and the barium oxalate precipitated by the addition of a fragment or two of sodium acetate. Barium oxalate should now appear either as rosettes of thin prisms or as radiates of long acicular crystals which are strongly birefringent; this reaction is not reliable when dealing with complex mixtures, especially as magnesium may mask the reaction.

Ammonium hydroxide reprecipitates all three oxalates from their solutions in dilute HCl or HNO<sub>3</sub>.

From hot solutions BaC<sub>2</sub>O<sub>4</sub>·*n*H<sub>2</sub>O separates in strongly birefringent orthorhombic plates and tabular crystals which are six-sided; even when the plates are more or less dendritic, a six-sided habitus is apparent. Strontium oxalate precipitated hot is monoclinic, also separating in six-sided tablets having parallel extinction; but there are also formed eight-sided plates and much-elongated rhombs (thin prisms with oblique ends), whose acute angles are 36° to 37° and exhibit an extinction angle of about 11°.

Although Fe<sup>+++</sup> and Al<sup>+++</sup> have no appreciable influence upon the oxalate reaction for Ca<sup>++</sup> and Sr<sup>++</sup>, they completely change that obtained with Ba<sup>++</sup> because of the formation of a double salt (?) which separates in very long, hair-like crystals (trichites) both straight and curved; the phenomenon is very characteristic. With Fe<sup>+++</sup> the tufts are brown, with Al<sup>+++</sup> colorless (brownish if very fine [structural color]). H<sub>2</sub>PtCl<sub>6</sub> induces the formation of less striking trichites.<sup>11</sup>

The presence of acetic acid facilitates the separation of typical crystals of calcium oxalate, retards the separation of strontium oxalate, and may entirely inhibit the separation of barium oxalate.

The oxalates of all three alkaline earths are readily soluble in dilute HCl and in dilute HNO<sub>3</sub>, but are reprecipitated by NH<sub>4</sub>OH. All three are converted into sulphates by dilute H<sub>2</sub>SO<sub>4</sub>.

Magnesium oxalate separates from solutions strongly acidulated with HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> in forms that are indistinguishable from those of calcium oxalate. If in doubt, decant, wash the oxalate crystals, dissolve in dilute HCl or HNO<sub>3</sub>, and add NH<sub>4</sub>OH in excess. The oxalates of the alkaline earths will be reprecipitated, but the oxalate of magnesium will

<sup>11</sup> A similar formation of trichiten crystals takes place when calcium is precipitated as oxalate in the presence of palladium chloride in acid solutions. Instead of the tiny tetragonal octahedra of the salt CaC<sub>2</sub>O<sub>4</sub>·3 H<sub>2</sub>O, long hair-like crystals with tufted ends are obtained. In the presence of palladium, strontium behaves similarly; but barium yields rods only, no trichites.

not. Magnesium oxalate is not precipitated in solutions containing a small amount of ammonium chloride.

$\text{Ag}^+$ ,  $\text{Cu}^+$ ,  $\text{Be}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Pb}^{++}$ ,  $\text{Sn}^{++}$ ,  $\text{Sn}^{++++}$ ,  $\text{Sb}^{+++}$ ,  $\text{Bi}^{+++}$ ,  $\text{Mn}^{++}$ , and the rare earths may each and all, under certain conditions, yield crystals so closely resembling the oxalates of  $\text{Ca}^{++}$  and  $\text{Sr}^{++}$  as to render it a difficult task to distinguish between them without having recourse to determination of their optical constants.

Oxalic acid must, therefore, be regarded as a reagent whose chief usefulness is that of merely indicating the presence or absence of a number of elements. It is rare indeed that it can be employed for positive identification.

In the presence of alkali oxalates, double oxalates may be formed of sufficiently low solubility as to bring about a separation of more or less well-formed crystals in the test drop. The elements which most often give rise to the separation of double oxalate crystals are: thallium, uranium, manganese, antimony, bismuth, iron, nickel, cobalt, and palladium.

In spite of its obvious limitations, precipitation of the alkaline earths as oxalates has its advantages, for it serves to indicate the presence of calcium, strontium, and barium in mixtures containing trivalent metals, borates, and many complexes where other reagents sometimes fail to yield a satisfactory crystalline precipitate.

A most curious anomaly in the habits of the alkaline-earth oxalates when formed in the presence of stannic chloride (chlorostannic acid) was pointed out by Behrens many years ago. Although we know of no other compound similarly affecting the crystallization of these oxalates, it is reasonable to suppose that others exerting a similar action probably exist. So striking and characteristic is the change in habit produced by  $\text{H}_2\text{SnCl}_6$  that this can be employed to distinguish between calcium, strontium, and barium.

This modified test can be performed as follows. To the neutral, moderately concentrated test drop add a very little  $\text{H}_2\text{SnCl}_6$ ; stir thoroughly. At the center of the drop thus prepared add a fragment of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . In a few seconds, instead of the usual oxalate crystals, there will be seen, if calcium is present, tiny rounded grains and thin disks. Some of the grains show evidences of being octahedra with rounded edges and rounded angles. They are smaller than  $\text{CaC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$  crystals obtained with pure calcium salts. Strontium forms at once *large, brilliant*, well-developed tetragonal octahedra; but these beautiful crystals soon become corroded, crumble into fine powder, and gradually disappear. Instead of its usual branching forms, barium gives clean-cut rectangular prisms terminating in pyramids, prisms tapering to a point, and masses of prisms with obliquely truncated ends. If much barium is present, long, very pointed, fusiform crystals, singly or in radiating masses, or bundles of very slender pointed needles, are obtained.

The solubilities of the oxalates of calcium, strontium, and barium in water at room temperature are not direct functions of the atomic weights of the elements. The calcium salt is the least soluble of the three and the strontium salt the most soluble.

Zinc yields  $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  in tiny pseudo-octahedra usually united in two's, or double spherulites resembling dumb-bells, but thin rhombs or short, stout rods with rounded ends are sometimes formed

(Fig. 84, page 119). Few crystals of zinc oxalate show distinct angles. When single octahedra are obtained, their resemblance to calcium and to strontium oxalates is such as to lead to confusion. The oxalate test for zinc is unreliable in mixtures.

Cadmium gives long, thin, colorless monoclinic prisms with obliquely truncated ends; singly, in X's, or in irregularly radiating groups (Fig. 85, page 119). This salt has the formula  $\text{CdC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$ , but from concentrated solutions well-formed octahedra separate that are not distinguishable from the oxalates of zinc, calcium, or strontium. The presence of calcium, strontium, or zinc prevents the formation of the prismatic type of cadmium oxalate.

Manganous salts form  $\text{MnC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$  in long slender prisms or six-armed, star-like groups; the latter result from the intersection of twinned prisms (Fig. 89, page 119). Manganous oxalate is strongly birefringent with parallel extinction. The best crystals are obtained when the dilute test drop is acidified with acetic acid. Free mineral acids must be absent. Good results are obtainable only when manganous salts are present in considerable excess compared with the salts of other elements precipitable by oxalic acid.<sup>12</sup> (See Manganese, page 262.)

In spite of its ready solubility in water,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$  may separate in the test drop, on standing, in long slender prisms or in foliated plates, less frequently in asymmetric, six-sided, many-faced tablets. The crystals are monoclinic but their common orientation on the object slide is such that they exhibit parallel extinction. Their birefringence is strong and negative. Rhombiform plates have acute angles of approximately  $53^\circ$ . Thin six-sided tablets have terminal plane angles of  $119^\circ$ . Test drops should be studied before concentrations reach a state permitting the separation of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ .

Since oxalic acid (or an acid alkali oxalate) gives a precipitate with a large number of elements, it is essential that the analyst confirm his findings by several other tests. Errors are less liable to be made if the analyst consults the following table of oxalates most frequently precipitated.

In the table on p. 120 only the commonly observed crystal forms have been listed as obtained by Method I at room temperature. In mixtures these crystal forms are ordinarily considerably modified;<sup>13</sup> the character of the changes in appearance is dependent upon the nature of the ions present and their relative concentrations.

<sup>12</sup> Both mercurous and mercuric salts are precipitated as oxalates of low solubility. The character of the precipitates varies with concentration, temperature, and acidity of solution, but it should not be forgotten that oxalic acid gives no precipitate with solutions of mercuric chloride or bromide.

<sup>13</sup> See Whitmore and Schneider: *Mikrochemie* 8, 302 (1930).

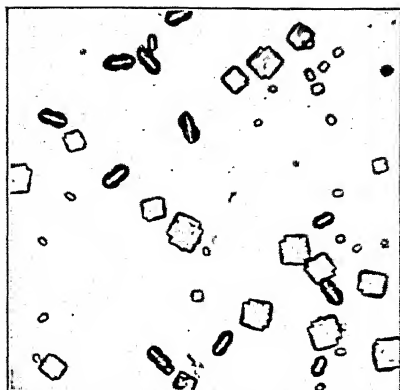


FIG. 84. Zinc with Oxalic Acid.  
300X.

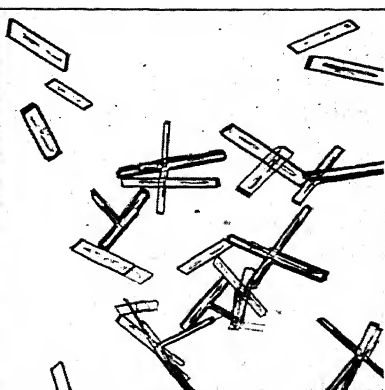


FIG. 85. Cadmium with Oxalic Acid.  
100X.



FIG. 86. Bismuth with Potassium  
Oxalate. 200X.

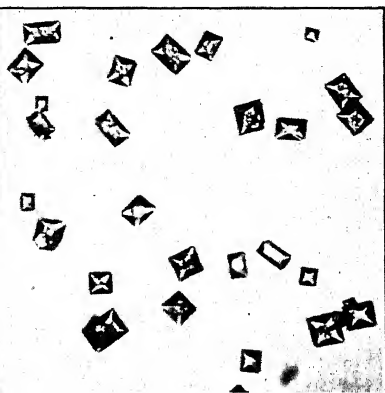


FIG. 87. Bismuth with Potassium  
Oxalate. 400X.

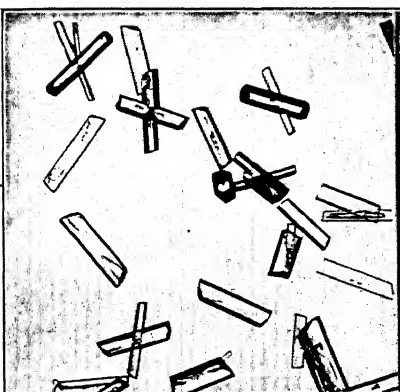


FIG. 88. Tin ( $\text{Sn}^{++}$ ) with Potassium  
Oxalate. 100X.

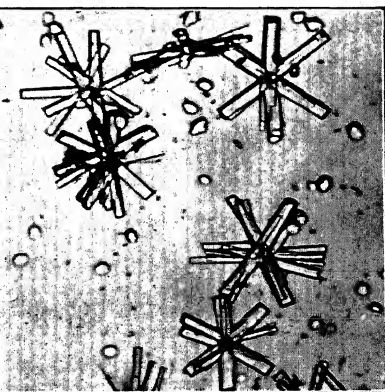


FIG. 89. Manganese ( $\text{Mn}^{++}$ ) with  
Potassium Oxalate. 100X.

*The precipitate consists of:**Possible presence of the elements grouped below:*

Granules or is pulverulent  
"Octahedral" crystals

Ag; Pb; Bi; Rare Earths; Ni; Hg  
Ca; Sr; (Ba); Zn; Cd; Zr; Mg; Pb;  
Mn; Bi

Spherulites or disks

Ag; Zn; Cd

Trichites

Ba with Fe or Al; Ca or Sr with Pd

Dendritic masses

Pb; Sn; Hg; Ba; Mn

Prisms, plates

Ag; Tl<sup>+</sup>; (Be); Zn; Cd; Pb<sup>++</sup>; Sn<sup>++</sup>,  
Fe<sup>++</sup>, Mn<sup>++</sup>; U; Bi

Slender prisms, fine needles or rods,  
singly or in groups or radiates

(Be); Cd; Pb<sup>++</sup>; Sb; Bi; Sn; Rare  
Earths; Mn<sup>++</sup>; Rh; Pd; Hg; Ba

**Experiments.**

(a) Try the reaction with oxalic acid after the manner given above, on a salt of Ca in a neutral solution. Try again in the presence of a strong acid.

(b) Precipitate  $\text{CaC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ , draw off the supernatant liquor, and treat the residue with dilute  $\text{H}_2\text{SO}_4$ . After examining the preparation, add more acid, and heat until white fumes appear; cool; breathe upon the preparation, and examine again.

(c) Test a drop of  $\text{SrCl}_2$  solution with  $\text{H}_2\text{C}_2\text{O}_4$ .

(d) Treat the oxalate thus obtained with  $\text{H}_2\text{SO}_4$  and recrystallize.

(e) Test a salt of Ba with  $\text{H}_2\text{C}_2\text{O}_4$ , in both hot and cold solutions.

(f) Make a mixture of Ca, Sr, Ba. Add  $\text{H}_2\text{C}_2\text{O}_4$ . Repeat the experiment in  $\text{HNO}_3$  solution; after a few minutes, decant the clear solution, concentrate slightly, and add  $\text{NaC}_2\text{H}_3\text{O}_2$ .

(g) Try the effect of the presence of  $\text{FeCl}_3$  on the precipitation of oxalates of Ca, Sr, Ba; first each element separately, then in mixtures of Ca and Ba; Sr and Ba; Ca, Sr, and Ba.

(h) Try  $\text{H}_2\text{C}_2\text{O}_4$  on a salt of Mg; then add an excess of  $\text{HC}_2\text{H}_3\text{O}_2$  to the test drop and examine again.

(i) Test salts of Zn, Cd, Bi, Pb, and Ag.

(j) To a test drop containing Ca and  $\text{SnCl}_2$ ; add oxalic acid. Compare the oxalate obtained with Ca oxalate formed in the absence of  $\text{SnCl}_2$ .

(k) Repeat the experiment with a salt of Sr. With a salt of Ba.

**E. By Means of Sodium Tartrate Acidified with Tartaric Acid —**  
 $\text{HNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O} + \text{H}_2\text{C}_4\text{H}_4\text{O}_6.$

*Compounds Formed* —  $\text{Ca}(\text{C}_4\text{H}_4\text{O}_6) \cdot 4\text{H}_2\text{O}$

$\text{Sr}(\text{C}_4\text{H}_4\text{O}_6) \cdot n\text{H}_2\text{O}$

$\text{Ba}(\text{C}_4\text{H}_4\text{O}_6) \cdot n\text{H}_2\text{O}.$

The application of the reagent by Method I, page 31, appears to be the most satisfactory for the production of characteristic crystals having the probable composition given above. Both the test drop and that of the reagent must have a concentration greater than is commonly employed in microscopical qualitative analysis. But it is essential that calcium shall be in excess of sodium in order to reduce as far as possible the danger of the formation of a double tartrate of sodium and calcium.

Addition of a *very small amount* of acetic acid is desirable as it aids the formation of well-developed characteristic crystal forms. Free mineral acids must be absent.

In preparing the reagent drop, sufficient acetic acid should be added to make the solution decidedly acid; but a great excess is to be avoided since the solubilities of the Ca, Sr, and Ba tartrates are thereby appreciably increased.

Calcium tartrate is readily soluble in solutions containing NaOH, KOH,  $\text{NH}_4\text{Cl}$ , and dilute acetic acid, but is practically insoluble in glacial acetic acid.

$\text{Ca}(\text{C}_4\text{H}_4\text{O}_6) \cdot 4 \text{H}_2\text{O}$  separates slowly in the form of large, colorless, brilliant, strongly birefringent orthorhombic prisms, with obliquely truncated ends (Fig. 72, page 109), singly, in clusters, and in masses. Characteristic penetration twins are frequent.

In dilute solutions the crystals appear only after a long time, while on the other hand, if the test drop is too concentrated, non-characteristic prisms and crystallites are precipitated.<sup>14</sup>

Strontium forms a similar compound, isomorphous with the calcium salt and not readily distinguishable from it, even though it has a tendency to form shorter, stouter prisms.

Barium yields an immediate precipitate in the form of a very fine powder.

Lead tartrate is first precipitated in a fine granular condition. Soon, however, irregular bristly masses and crystallites are formed, whose appearance is quite different from the tartrates of calcium and strontium.

Much magnesium seriously interferes with the formation of typical tartrates of calcium and strontium and their habit may be greatly modified.<sup>15</sup>

The appearance and properties of the tartrates of the alkali metals have already been discussed on pages 72, 73.

Calcium sulphate heated in a solution of alkali tartrate is converted into calcium tartrate, which is readily soluble in dilute HCl. This reaction can be turned to advantage when dealing with a mixture of the sulphates of calcium, strontium, and barium, for the sulphates of strontium and barium are unaffected by heating with sodium tartrate or with sodium potassium tartrate.

Testing complex mixtures for calcium by the tartrate method is of

<sup>14</sup> According to Chattaway: *Jour. Amer. Chem. Soc.*, 38, 2519 (1916), the crystals first formed are those of the hexagonal salt  $\text{CaC}_4\text{H}_4\text{O}_6 \cdot 6 \text{H}_2\text{O}$ . This metastable salt rapidly loses  $2 \text{H}_2\text{O}$  and becomes the orthorhombic stable tetrahydrate.

<sup>15</sup> Behrens-Kley: *Mikrochemische Analyse*, p. 52.

little value, since well-formed characteristic crystals are obtainable with comparatively pure salts of calcium only; but with salts of calcium in the absence of strontium, barium, lead, and thallium the reaction is characteristic and leaves little to be desired. The formation of calcium tartrate constitutes a valuable reaction for the identification of tartaric acid.

#### Experiments.

- (a) Test a salt of Ca.
- (b) Repeat, having a strong acid present. Then repeat, having  $\text{NH}_4 \cdot \text{C}_2\text{H}_3\text{O}_2$  present.
- (c) Test salts of Sr and Ba.
- (d) Test a mixture of Ca and K.

#### F. By Means of Ammonium Bichromate — $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ .

*Compounds Formed* —  $\text{SrCrO}_4$   
 $\text{BaCrO}_4$ .

To the dilute test drop containing no free mineral acid but strongly acidified with acetic acid, apply the reagent by Method II, page 33.

Barium chromate separates at once in the form of minute grains, square or rectangular plates, and tablets. Some preparations exhibit minute rods, singly and in crosses, and X's which on standing may become slightly dendritic. A high magnification is always necessary for the resolution of the crystals formed.

When applying this test, be sure the test drop is dilute with respect to the alkaline earths. Do not stir the preparation after the fragment of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  has been introduced, and avoid rubbing the glass with a glass rod or platinum wire. Rubbing causes an instantaneous precipitation of  $\text{BaCrO}_4$  in so finely divided a condition as to render it amorphous in appearance. Moreover, other chromates are more likely to be precipitated, especially if the test drop is moderately concentrated. Allow to stand for some time to insure the separation of as much  $\text{BaCrO}_4$  as possible.

Chromates of  $\text{Ag}^+$ ,  $\text{Pb}^{++}$ ,  $\text{Hg}^+$ ,  $\text{Hg}^{++}$ ,  $\text{Tl}^+$ , and certain organic bases are also precipitated in acetic acid solutions and these inorganic cations also yield a precipitate in solutions acidified with  $\text{HNO}_3$ , whereas  $\text{BaCrO}_4$  is soluble in  $\text{HNO}_3$  and in  $\text{HCl}$ . Differentiation of simple salts is thus possible, but in mixtures separations are necessary before identification tests are applied.

Carefully decant the mother liquor. Into the decanted, clear drop cause a drop of  $\text{NH}_4\text{OH}$  to flow;  $\text{SrCrO}_4$  will be precipitated in tiny yellow globulites or dumb-bell-shaped aggregates; short stout fusiform bodies are also formed. If the original acetic acid test drop is suffi-



ciently dilute, no precipitate should be produced if only  $\text{Sr}^{++}$  and  $\text{Ca}^{++}$  are present.  $\text{Ca}^{++}$  gives no precipitate in either neutral, acid, or alkaline solutions.

$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (or  $\text{K}_2\text{Cr}_2\text{O}_7$ ) is used as reagent rather than  $\text{K}_2\text{CrO}_4$  because the latter reagent may precipitate  $\text{SrCrO}_4$  even in dilute acetic acid solution in forms not distinguishable from those of  $\text{BaCrO}_4$ , save that the crystals are often much larger. Bichromates thus afford a convenient separation of  $\text{Ca}^{++}$ ,  $\text{Sr}^{++}$ , and  $\text{Ba}^{++}$ .

After  $\text{SrCrO}_4$  has been precipitated by the addition of  $\text{NH}_4\text{OH}$ , decantation can again be practiced and to the decanted solution  $\text{H}_2\text{SO}_4$  or  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  added to test for the presence of calcium; or the preparation may be evaporated to complete dryness and extracted with alcohol. Calcium chromate is soluble in alcohol but strontium chromate and barium chromate are insoluble.

#### Experiments.

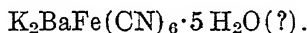
(a) Try the bichromate reaction on salts of Ba, Sr, and Ca.

(b) Try mixtures of Ca and Ba, Sr, and Ba; use solutions acidified with  $\text{HC}_2\text{H}_3\text{O}_2$ , decant the clear solution, and to it add  $\text{NH}_4\text{OH}$ .

(c) Try the reagent upon Ba and Sr salts in  $\text{HNO}_3$  solution. Then try it upon Ag, Pb, and mercurous salts in  $\text{HNO}_3$  solution.

#### G. By Means of Potassium Ferrocyanide — $\text{K}_4\text{Fe}(\text{CN})_6$ .

*Compounds Formed* —  $\text{K}_2\text{CaFe}(\text{CN})_6 \cdot 3 \text{H}_2\text{O} (?)$ <sup>16</sup>



Apply the reagent by Method I, page 31, to a moderately concentrated test drop which has been acidified with  $\text{HC}_2\text{H}_3\text{O}_2$  and to which a *very little*  $\text{NH}_4\text{Cl}$  has been added.

Free mineral acids must be absent; it is therefore advisable always to add a little  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  to the test drop.

Calcium yields, almost immediately, tiny, practically colorless tetragonal crystals in the form of square and rectangular plates, many of them with beveled corners (Fig. 68, page 105).

If the concentration is too high with respect to  $\text{Ca}^{++}$ , a granular precipitate is formed; and, if much  $\text{NH}_4\text{Cl}$  or  $\text{KCl}$  is present, a very insoluble salt may be precipitated. This salt has been considered to have the formula  $\text{K}_2\text{CaFe}(\text{CN})_6 \cdot 4 (\text{NH}_4)_2\text{CaFe}(\text{CN})_6$  and separates in pulverulent form only. More recent investigations, however, appear to cast some doubt on its existence.<sup>17</sup>

<sup>16</sup> According to Karaoglanov: *Zeit. anorg. allg. Chem.* 229, 313 (1936), these salts are anhydrous.

<sup>17</sup> Chandelle: *Bul. soc. chim. Belg.* 41, 420 (1932), believes that not a triple salt is

Strontium gives no reaction save in very concentrated solutions, and then only as a fine granular deposit.

Barium forms large, faintly yellow crystals of the moderately soluble orthorhombic salt  $\text{K}_2\text{BaFe}(\text{CN})_6 \cdot 5 \text{H}_2\text{O} (?)$  of characteristic habit, in clear, transparent rhombs and rhombic tablets; the smaller equilateral rhombs exhibit symmetrical extinction (Fig. 69, page 105). A triclinic modification  $\text{K}_2\text{BaFe}(\text{CN})_6 \cdot 3 \text{H}_2\text{O} (?)$  is also known and may separate in the test drop if conditions are favorable for the formation of the metastable form.

The reagent  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3 \text{H}_2\text{O}$  forms monoclinic crystals which under certain conditions may lead to confusion with the  $\text{Ba}^{++}$  double salt, if the test drop is allowed to evaporate until the concentration is such that the reagent begins to crystallize out.

If the test drop is alkaline, a potassium-magnesium ferrocyanide may be precipitated, which closely resembles the calcium salt, but no separation takes place in acid solutions nor in solutions containing moderate quantities of ammonium salts.

$\text{K}_4\text{Fe}(\text{CN})_6$  precipitates many other elements as well as calcium and barium; most of these precipitates are heavy, voluminous, and non-crystalline. In this list of insoluble or very difficultly soluble ferrocyanides, the most frequently met with are those of lead, zinc, iron, copper, mercury, uranium, titanium, gallium, and some of the rare earths; of these the ferrocyanides of copper and uranium are brown; those of iron, blue.

### Experiments.

(a) Crystallize a little of the reagent  $\text{K}_4\text{Fe}(\text{CN})_6$ , alone, and determine its optical properties.

(b) Try the test on pure salts of Ca, Sr, Ba, using both dilute and concentrated solutions.

(c) Try the reagent on mixtures of Ca and Sr, Ca and Ba, Sr, and Ba.

(d) Try the effect of the reagent on salts of Pb, Zn, and Fe. Then make mixtures of Ba and these elements and test.

### H. By Means of Arsenic Acid — $\text{H}_3\text{AsO}_4$ .

*Compounds Formed* —  $\text{NH}_4\text{CaAsO}_4 \cdot 6 \text{H}_2\text{O}$ .

To the drop to be tested, add sufficient  $\text{NH}_4\text{OH}$  to make it neutral or very slightly alkaline. Cause to flow in (Method I, page 31) an

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formed but two separate salts, to which he ascribes the formulas  $(\text{NH}_4)_4\text{Ca}_2\text{Fe}_2(\text{CN})_{12}$  and  $\text{Ca}_4\text{Fe}(\text{CN})_{12}$ .

See also Schoorl: *Beiträge z. Mikrochem. Anal.*, p. 122.

Flanders: *Jour. Amer. Chem. Soc.* 28, 1510 (1906).

Dains: *ibid.* 29, 727 (1907).

ammoniacal solution of ortho-arsenic acid. A heavy granular precipitate is at once formed.

If barium is present, the precipitate remains granular; no crystals develop therefrom.

If strontium is present, the granular deposit soon changes into minute stars and tiny disks.

But in the case of calcium, very large, colorless skeleton crystals of the salt  $\text{NH}_4\text{CaAsO}_4 \cdot 6 \text{H}_2\text{O}$  soon appear (Fig. 73, page 109). These crystals take the shape of elongated, somewhat distorted X's; in time they fill out and simulate envelopes or even grow into prisms of the orthorhombic system, with faces reminding one of the roofs of houses. The forms assumed are identical with those of  $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$  described on page 131, but the skeletal crystals are usually larger and the prisms less abundant. (See Fig. 77, page 109.)

Since most arsenates and phosphates of similar elements are isomorphous, it is to be expected that those cations which yield crystalline simple or double phosphates will also yield crystalline arsenates. Furthermore, if soluble phosphates produce a precipitate with a given cation, an analogous reaction may be expected with  $\text{H}_3\text{AsO}_4$  in ammoniacal solution. The usefulness of this reaction is obviously greatly restricted, and it is applicable in the group of the alkaline earths to relatively pure salts of calcium only.

Magnesium gives  $\text{NH}_4\text{MgAsO}_4 \cdot 6 \text{H}_2\text{O}$  identical in habit with the calcium salt. The zinc and cadmium salts are isomorphous with the magnesium salt, and, while not so readily obtained in good crystals, may under favorable conditions yield all the crystal forms normally obtained with calcium or magnesium.

Silver yields  $\text{Ag}_3\text{AsO}_4$  in characteristic deeply colored dendrites, skeletal forms, and tabular crystals, soluble in excess of  $\text{NH}_4\text{OH}$ . (See Silver, page 282.)

The importance of the  $\text{H}_3\text{AsO}_4$  reaction is chiefly with reference to the ion  $\text{AsO}_4^{3-}$ . When this ion occurs in solutions of complex mixtures, difficultly soluble, more or less crystalline double arsenates are prone to separate in the performance of various "micro" tests for both cations and anions.

#### I. By Means of Iodic Acid — $\text{HIO}_3$ .<sup>18</sup> ✓

*Compounds Formed* —  $\text{Ca}(\text{IO}_3)_2 \cdot 6 \text{H}_2\text{O}$

$\text{Sr}(\text{IO}_3)_2 \cdot 6 \text{H}_2\text{O}$

$\text{Ba}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ .

Iodic acid affords an excellent means of differentiating between salts

<sup>18</sup> Denigès: *Compt. rend.* 170, 996 (1920); *Bul. Soc. Chim.* (4), 27, 560 (1920).

of calcium, strontium, and barium, providing the salts are fairly pure and the test is made upon dilute solutions containing no free mineral acid. Thallium, lead, and silver must be absent as also compounds which can reduce iodic acid and iodates.

Apply the reagent by Method I, page 31. According to Denigès, the best results are obtained when the reagent is employed in approximately 10 per cent solution.

With salts of calcium there is slowly formed a very fine precipitate of almost colloidal dimensions; this gradually becomes granular, and appears brown or black in color by transmitted light. If the conditions of concentration are just right, tiny pointed bipyramids (pseudo-octahedra) or rhombs result. Well-formed crystals are rarely obtained; ordinarily, only ill-defined disks and more or less flattened spherocrystals separate; the latter on standing become drusy.

At room temperature, in neutral solution, the salt  $\text{Ca}(\text{IO}_3)_2 \cdot 6 \text{H}_2\text{O}$  separates, but from hot solutions or solutions containing free  $\text{HNO}_3$  a monohydrated salt is obtained. The hexahydrate has been variously ascribed to both the orthorhombic and the triclinic systems.

Strontium yields a fine granular precipitate, resembling that given by calcium, but this soon changes into masses of slender acicular crystals or slender triclinic (?) prisms of  $\text{Sr}(\text{IO}_3)_2 \cdot 6 \text{H}_2\text{O}$ ; the former are grouped in moss-like radiating tufts. The mossy effect is enhanced by many curving bundles of dendritic crystals. By transmitted light these bundles and masses appear brown or black but are snow-white by reflected light. From more concentrated solutions, dumb-bell-like masses and spherocrystals are obtained (Fig. 67, page 105) and occasionally short rods, singly or in X's or even short stout "octahedra" or forms closely resembling those given by calcium. If calcium is also present, the mossy clumps are not obtained.

As in the case of calcium, the monohydrated salt  $\text{Sr}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$  is precipitated in hot solutions and in solutions acidified with  $\text{HNO}_3$ .

Barium gives, instantaneously, a heavy white pulverulent precipitate unless the test drop is very dilute with respect to  $\text{Ba}^{++}$ . In the latter case clumps of characteristic radiating, curving acicular crystals of  $\text{Ba}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$  (monoclinic) are obtained (Fig. 66, page 105), quite different in appearance from the mossy masses of the strontium iodate; but if either calcium or strontium is present the test for barium fails.

Magnesium iodate,  $\text{MgIO}_3 \cdot 4 \text{H}_2\text{O}$  (monoclinic), is too soluble to separate unless the test drop goes completely to dryness; the same is true of lithium iodate.

Both zinc and cadmium give small brownish disks similar to those formed by calcium and by strontium; these disks develop into spherocrystals.

crystals, single, in two's, and in botryoidal masses which appear jet black by transmitted light. Rarely, individual and clumps of very fine acicular crystals are obtained.

The majority of the other commonly occurring heavy metals give with iodic acid heavy, white curdy or granular precipitates that appear brown or black by transmitted light with low-power objectives; under exceptionally favorable circumstances, disks, spherocrystals, or botryoidal masses may be obtained.

The only ions which yield *well-formed* crystalline iodates are  $\text{Sr}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Tl}^+$ , and  $\text{Ag}^+$ , and the radical  $\text{NH}_4^+$ . Thallous iodate separates in tiny crosses and dendritic rosettes of characteristic habit, white by reflected light, black by transmitted light. Silver gives fine, very slender needles, resembling  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  (but not grouped like gypsum) which show a tendency to form star-like radiating masses.

Lead nitrate in solution not acidified with nitric acid yields an instantaneous white, finely granular precipitate which does not become noticeably crystalline on standing. However, if the test drop has been acidified with nitric acid, the granular precipitate which is first formed may change into spherulites, dendrites, and skeletal forms or into fine acicular crystals, singly or in sheaves or bristly clumps. These crystals appear to be black by transmitted light. Bismuth and some salts of copper react in a similar manner.

Satisfactory iodate tests, as stated above, can be obtained with pure salts only. With mixtures the amorphous-appearing precipitated iodates either mask the reactions for  $\text{Sr}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Tl}^+$ ,  $\text{Ag}^+$ , and  $\text{NH}_4^+$  or prevent the separation of recognizable crystals.

### Experiments.

(a) Test with  $\text{HIO}_3$  salts of Ca, Sr, and Ba.

### J. Other Reactions of the Alkaline Earths.

#### 1. With *Fluosilicic Acid*.

See Sodium, page 63.

#### 2. With *Potassium Antimonyl Tartrate*.

See Antimony, page 238.

#### 3. With *Concentrated Hydrochloric Acid*.

The material to be tested is treated with strong  $\text{HCl}$  and the solution concentrated.

$\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$  is far less soluble, especially in  $\text{HCl}$ , than are Sr, Ca, and Mg chlorides. It separates as monoclinic plates and tables, almost rectangular in symmetry ( $\beta = 89^\circ$ ), and usually with one or more corners truncated by shaded faces to give a six- or eight-sided outline. Low-order polarization colors are exhibited by the plates, with an

extinction angle of about  $37^\circ$ , as measured with reference to the longer parallel bounding faces of the pseudo-rectangular tablets. Edge views of the plates, when obtainable, give parallel extinction. Some crystals show internal twinning, being divided along their diagonal into two halves which extinguish at different positions.

## SUMMARY OF SEPARATION METHODS FOR ALKALINE EARTHS

### *I. Separation based on different solubilities of alkaline earth sulphates.*<sup>19</sup>

Precipitate  $\text{Ca}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Ba}^{++}$  as sulphates. Filter or centrifuge. Extract the precipitate with hot dilute  $\text{HCl}$ .  $\text{CaSO}_4$  is readily soluble,  $\text{SrSO}_4$  slightly soluble,  $\text{BaSO}_4$  insoluble. Evaporate the  $\text{HCl}$  solution;  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  separates (Figs. 70, 71, page 105). The insoluble sulphates are dried, taken up on a platinum loop, and reduced to sulphides by heating in the reducing flame of a gas burner. The sulphides thus obtained are dissolved in dilute  $\text{HCl}$ . A portion is tested for  $\text{Ba}^{++}$  with  $(\text{NH}_4)_2\text{SiF}_6$  (see page 64). In the remaining  $\text{HCl}$  solution the  $\text{Ba}$  is removed with  $\text{K}_2\text{CrO}_4$ . Filter or centrifuge, and test the filtrate for  $\text{Sr}^{++}$  with  $\text{KIO}_3$ . (See page 126.)

### *II. Separation based on treatment of alkaline-earth carbonates.*<sup>20</sup>

Dissolve the carbonates in a concentrated solution of ammonium acetate. To the clear solution add a saturated solution of  $\text{K}_4\text{Fe}(\text{CN})_6$ ; the calcium is precipitated as  $\text{Ca}(\text{NH}_4)_2\text{Fe}(\text{CN})_6$ ;  $\text{Sr}^{++}$  and  $\text{Ba}^{++}$  do not interfere unless the solution is too highly concentrated. (See page 123.) Filter or centrifuge. In the clear solution, precipitate the  $\text{Ba}^{++}$  in the cold with  $\text{Na}_2\text{SO}_4$ , filter or centrifuge, boil the filtrate;  $\text{SrSO}_4$  is precipitated.

### *III. Separations based upon the use of organic solvents.*

A.<sup>21</sup> To the solution to be tested add several cubic centimeters of acetone and of 9 *N* ammonium carbonate. Allow to stand with frequent stirring. Filter, wash precipitate with  $(\text{NH}_4)_2\text{CO}_3$  solution. Dissolve the precipitated carbonates in dilute acetic acid, carefully avoiding an excess. Add 2 cc. 6 *N* acetic acid and 3 cc. of 3 *N* ammonium acetate. Concentrate to small bulk. Add  $\text{K}_2\text{CrO}_4$  solution to complete precipitation of  $\text{Ba}^{++}$ . Heat to boiling; filter. To the filtrate add sufficient concentrated  $\text{NH}_4\text{OH}$  to change its color to orange. Add acetone, a little at a time, with constant stirring; a yellow precipitate

<sup>19</sup> Brintzinger and Brintzinger: *Zeit. anal. Chem.* 94, 166 (1933).

<sup>20</sup> Schienkmann and Politzschuck: *Zeit. anal. Chem.* 94, 192 (1933).

<sup>21</sup> Williams and Briscoe: *Chem. News* 145, 177 (1932).

indicates strontium. Filter, dilute the filtrate, and add a small volume of 3 *N* ammonium oxalate; if a precipitate forms, add sufficient reagent to precipitate all the  $\text{Ca}^{++}$  as  $\text{Ca}(\text{C}_2\text{O}_4)_2$ . Filter and in the filtrate precipitate  $\text{Mg}^{++}$  with  $\text{HNa}_2\text{PO}_4$ .

The series of precipitates obtained should be subjected to microscopical examination for confirmation and may be converted into other characteristic compounds if the analyst is still in doubt.

*III-B.* Convert carbonates to chlorides. Evaporate to complete dryness. Extract with amyl alcohol or absolute ethyl alcohol:  $\text{CaCl}_2$  and  $\text{SrCl}_2$  are soluble,  $\text{BaCl}_2$  is insoluble.<sup>22</sup> Evaporate the solvent, dissolve the residue in water, and precipitate  $\text{Ca}^{++}$  and  $\text{Sr}^{++}$  as chromates. Filter and dry the precipitate and extract it with alcohol. Calcium chromate is soluble, strontium chromate insoluble. In the aqueous filtrate from the chromate precipitation  $\text{Mg}^{++}$  can be precipitated as  $\text{MgNH}_4\text{PO}_4$ .

*III-C.* Somewhat similar principles are involved in a separation suggested by Yagoda.<sup>22</sup>

Chlorides of the alkalis and alkaline earths are converted into bromides by treatment with 8 *N* hydrobromic acid.

Na, K, Ba bromides are separated from Mg, Sr, Ca bromides by extraction with isoamyl alcohol.

Convert the Na, K, Ba bromides into chlorides by 12 *N* hydrochloric acid; separate KBr by extraction with ethyl alcohol.

Mg is separated from Ca and Sr by ignition of nitrates.

Ca is separated from Sr by solution of the calcium nitrate in 16 *N* nitric acid.

*III-D.* Dissolve the carbonates in acetic acid. Precipitate the  $\text{Ba}^{++}$  as chromate. Filter. In the filtrate reprecipitate  $\text{Ca}^{++}$  and  $\text{Sr}^{++}$  as carbonates with  $(\text{NH}_4)_2\text{CO}_3$  and dissolve this precipitate in dilute  $\text{HNO}_3$ ; evaporate the nitrate solution to complete dryness. Extract the nitrate residue with a mixture of equal parts ether and alcohol.<sup>23</sup>  $\text{Ca}(\text{NO}_3)_2$  is soluble,  $\text{Sr}(\text{NO}_3)_2$  only very slightly soluble,  $\text{Ba}(\text{NO}_3)_2$  is insoluble. Evaporate the ether-alcohol extract, dissolve the residue in water, test for  $\text{Ca}^{++}$ . The residue which was insoluble in ether-alcohol is tested for  $\text{Sr}^{++}$  and  $\text{Ba}^{++}$  by any of the procedures outlined above.

*III-E.* Dissolve the carbonates in dilute  $\text{HNO}_3$ . Evaporate to complete dryness and extract with acetone;  $\text{Ca}(\text{NO}_3)_2$  is soluble  $\text{Sr}(\text{NO}_3)_2$  and  $\text{Ba}(\text{NO}_3)_2$  insoluble. Evaporate the acetone extract, dissolve the

<sup>22</sup> Browning: *Amer. Jour. Sci.* (3) 43, 50, 314 (1892).

Yagoda: *Jour. Amer. Chem. Soc.* 52, 3068 (1930).

<sup>23</sup> Stromeyer: *Ann. d. Physik* 54, 245 (1908).

residue in water, and test for  $\text{Ca}^{++}$  with  $\text{H}_2\text{SO}_4$ . (See page 106.) The residue which is insoluble in acetone is dried thoroughly, mixed with dry  $\text{NH}_4\text{Cl}$ , and heated for some time just below the subliming point of  $\text{NH}_4\text{Cl}$ , whereby the nitrates are converted into chlorides. The cold chlorides are extracted with alcohol;  $\text{SrCl}_2$  is soluble,  $\text{BaCl}_2$  insoluble. Evaporate the alcoholic extract, dissolve the residue in water, and test for  $\text{Sr}^{++}$ . The residue insoluble in alcohol is tested for  $\text{Ba}^{++}$ .

### DETECTION OF MAGNESIUM

The addition of  $\text{NH}_4\text{OH}$  to a  $\text{HCl}$  solution containing magnesium salts but no  $\text{NH}_4\text{Cl}$  causes the precipitation of about one half the  $\text{Mg}^{++}$  as  $\text{Mg}(\text{OH})_2$ , the other half remaining in solution as the double salt  $2\text{NH}_4\text{Cl} \cdot \text{MgCl}_2$ ; <sup>24</sup> ( $\text{Zn}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Fe}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ , behave similarly). In the presence of salts of ammonium no precipitate is usually obtained with  $\text{NH}_4\text{OH}$ .

$(\text{NH}_4)_2\text{CO}_3$  precipitates a basic carbonate in neutral solutions free from ammonium salts, providing the solution is boiled or allowed to stand a long time.

$\text{Ba}(\text{OH})_2$  precipitates  $\text{Mg}(\text{OH})_2$  quantitatively only in the absence of salts of ammonium.

Phosphates and arsenates precipitate magnesium quantitatively even in the presence of large amounts of ammonium salts.

**A. By Means of Uranyl Acetate** —  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ .

*Compound Formed* —  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot x\text{H}_2\text{O}$ .

This reaction has been discussed at length under Sodium, Method A, pages 54–58 (Fig. 33, page 53).

Note well that this triple acetate reaction (polysynthetic monoclinic twins) is also given by a number of other cations, whose absence must be proved before a decision can be reached as to the presence of magnesium.

**B. By Means of Sodium Phosphate** —  $\text{HNa}_2\text{PO}_4$  — in Ammoniacal Solution.

*Compound Formed* —  $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ .

Certain phases of this reaction and properties of the reaction product have been discussed under Ammonium, page 76.

The detection of magnesium in simple salts is easy, rapid, and certain, since crystals characteristic of magnesium are readily obtained; but the identification of this element in complex mixtures is apt to prove difficult, inasmuch as it is generally associated with other elements

<sup>24</sup> Denigès: *Compt. rend.* 175, 1206 (1922).



which form insoluble phosphates or hydroxides, and which interfere with, or mask, the test for magnesium.

To a large test drop of the moderately concentrated solution to be tested, add a few tiny fragments of  $\text{NH}_4\text{Cl}$ ; stir thoroughly, then add several fragments of citric acid; warm gently and stir until dissolved. Add a drop of a concentrated solution (or a fragment) of  $\text{HNa}_2\text{PO}_4$ . Warm gently and stir. Now cause a drop of a strong solution of  $\text{NH}_4\text{OH}$  to flow into the test drop, but do not warm again.

$\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$  is first precipitated in a more or less granular condition; this soon changes into dendritic forms and large feathery stars and X's (Fig. 76, page 109), which in turn develop into plates and tabular forms resembling envelopes and finally rectangular orthorhombic prisms, appear. Crystals recalling the roofs of houses are abundant and characteristic (Fig. 77, page 109). This salt is a striking example of the general analytical principle that "digestion" increases the size of a crystalline precipitate and facilitates filtration and washing.

If a precipitate is formed when the  $\text{HNa}_2\text{PO}_4$  is added, i.e., before making the test drop alkaline with  $\text{NH}_4\text{OH}$ , it is best to decant the supernatant liquid and add the  $\text{NH}_4\text{OH}$  to the decanted drop. The precipitate is set aside for subsequent analysis.

Insufficient  $\text{NH}_4\text{Cl}$  or citric acid may permit the formation of precipitates which may mask the reaction for magnesium. Too much  $\text{NH}_4\text{Cl}$  is objectionable.

The precipitate usually clings tightly to the glass, permitting easy decantation. After decanting, dissolve the precipitate in dilute  $\text{HCl}$ , in which it is very soluble, and reprecipitate with  $\text{NH}_4\text{OH}$ . Characteristic star-like and X-formed feathery crystals are obtained if the original crystals were  $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ . These dendritic and skeleton forms are more characteristic of  $\text{Mg}^{++}$  than the fully developed prismatic crystals.

Double ammonium phosphates of like habit and isomorphous with  $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$  are formed by  $\text{Fe}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ . Of these four elements Mn alone is precipitated (but only incompletely) by  $\text{NH}_4\text{OH}$  in the presence of citric acid (ammonium citrate) and unless present in large amount usually does not interfere with the recognition of Mg. If in doubt, decant, wash the precipitate, and cover the crystals with  $\text{H}_2\text{O}_2$ ; if Mn is present the crystals should turn brown.

In ammoniacal citrate solutions  $\text{HNa}_2\text{PO}_4$  will completely precipitate Mg, Ca, Sc, Pb, Au, rare earths, and partly precipitate Be, Sr, Ba, Hg, In, U, Zr, Mn.<sup>25</sup>

<sup>25</sup> Lundell and Hoffman: *Outlines of Methods of Chemical Analysis* (Wiley, New York, 1938), p. 70.

Granular or flocculent precipitates may be obtained from  $\text{Ca}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Sn}^{++++}$ ,  $\text{Pb}^{++}$ ,  $\text{Ag}^+$ ,  $\text{Cu}^+$ ,  $\text{UO}_2^{++}$ ,  $\text{Be}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Al}^{+++}$ ,  $\text{Li}^+$ , rare earths.

In acid solution there may also appear granular or sandy precipitates of phospho-molybdates, -tungstates, etc., but these should normally dissolve in  $\text{NH}_4\text{OH}$  and not interfere with the subsequent separation of  $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$ . It is always advisable to decant the solution from the precipitate formed, wash once, dissolve in dilute  $\text{HCl}$ , add citric acid, and reprecipitate with  $\text{NH}_4\text{OH}$ . More characteristic crystals are thus obtained and the possibilities of interferences are greatly reduced.

$\text{Li}^+$  should be absent (see page 88), for if present no satisfactory test for  $\text{Mg}^{++}$  can be obtained. Under such conditions precipitate the  $\text{Mg}^{++}$  with  $\text{Ba}(\text{OH})_2$ ,<sup>26</sup> filter, wash, dissolve the precipitate in very dilute acid, remove the Ba with  $\text{H}_2\text{SO}_4$ , and test the solution for  $\text{Mg}^{++}$ .

In the analysis of a mixture of absolutely unknown composition, it is usually essential that the search for  $\text{Mg}^{++}$  be deferred until other tests have been made, *e.g.*, with  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_4\text{OH}$ ,  $(\text{NH}_4)_2\text{CO}_3$ ,  $\text{H}_2\text{C}_2\text{O}_4$ , etc.

It may sometimes happen that  $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$  is precipitated when  $\text{NH}_4\text{OH}$  is added; if so, its characteristic crystal form will be recognized. It more frequently happens, however, that if both  $\text{Mg}^{++}$  and  $\text{PO}_4^{---}$  are present in a complex mixture other cations are also present which form difficultly soluble phosphates, and these phosphates are insoluble in  $\text{NH}_4\text{OH}$ ; under such conditions the detection of  $\text{Mg}^{++}$  becomes exceptionally difficult. Behrens' suggestion to remove  $\text{PO}_4^{---}$  by means of  $\text{SnO}_2$  formed from metallic tin is not always successful, but should be tried. Acidify with  $\text{HNO}_3$  (1 : 2), add a few bits of pure tin foil, and heat the preparation; as soon as the reaction has ceased, heat to boiling. Cool and extract the material with dilute  $\text{HNO}_3$ , filter, and test the filtrate as directed above. The treatment with tin and nitric acid is conveniently performed in the micro crucible. (See page 17.)

A variant of the phosphate test has been suggested by Martini and Schamis.<sup>27</sup> It consists in substituting cesium for ammonium. To the test drop,  $\text{HN}_2\text{PO}_4$  and  $\text{CsCl}$  are added. Tetrahedra of the salt  $\text{CsMgPO}_4 \cdot 6 \text{H}_2\text{O}$  are obtained. This procedure has no advantages over the production of  $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$ .

### Experiments.

(a) Try the phosphate reaction on a solution of  $\text{MgSO}_4$ ; then try it on salts of Fe, Mn, Co, Ni, Al, Zn, and Cd. Repeat the experiments, this time adding the  $\text{HN}_2\text{PO}_4$  after the  $\text{NH}_4\text{OH}$ .

<sup>26</sup> Schoorl: *Beiträge*, p. 130.

<sup>27</sup> *Second Chem. Congress Buenos Aires, 1924, 14.*

(b) Make mixtures, trying various combinations of the above with members of Groups I and II.

(c) Test for ammonia by means of this reaction as described on page 76.

C. By Means of Diphenylcarbazine<sup>28</sup>:  $\text{OC} \begin{cases} \text{NH} \cdot \text{NHC}_6\text{H}_5 \\ \text{NH} \cdot \text{NHC}_6\text{H}_5 \end{cases}$

This reaction described by Feigl as a "spot" test, specific for members of Group II, can be modified so as to be useful in microscopical qualitative analysis for the detection of several elements.

For the reactions described below the reagent should be prepared as follows: the diphenylcarbazine in a small heap five millimeters in diameter and one millimeter thick is placed in a small crucible (page 17) or very small test-tube; eight drops of alcohol are added, and the solution gently warmed to dissolve all the carbazine. Add powdered sodium hydroxide in an amount equal to about one half the volume of the dry carbazine. Stir until all has dissolved; then add five to seven drops of distilled water, stir thoroughly. The blood-red solution thus obtained should be employed at once since it rapidly undergoes an alteration which may render it useless in about three hours. It is always advisable to make a blank test with aluminum nitrate or chloride before undertaking an analysis of material of unknown composition. Aluminum salts should give, in a few seconds, compact spherulites made up of very fine, thin acicular plates or fine needles, brown by transmitted light. If, instead of these spherulites, tiny, thin transparent disks with a wavy outline (of the same appearance as the disks shown in Fig. 51, page 77) are obtained, the reagent is too concentrated and should be cautiously diluted; if too dilute, characteristic reactions cannot be obtained.

The material to be tested must contain no free acid and should be substantially neutral. Satisfactory reactions can be obtained by Method I, page 31, or by introducing into the drop of reagent a fragment of the material to be tested. When Method I is used, the test drop should be moderately concentrated. If the fragment of solid is to be introduced, the reagent drop should be large and the unknown a fragment about one millimeter in diameter.

The reaction is very sensitive for some cations but not for others; hence the reason for relatively large amounts when dealing with unknown materials.

Magnesium yields an intense rose-red "amorphous" precipitate

<sup>28</sup> Feigl: *Mikrochemie* 2, 186 (1924); *Monats.* 45, 63 (1924).

whose color is specific for  $\text{Mg}^{++}$ . Salts of tin prevent this reaction for magnesium.

Calcium yields an "amorphous" precipitate, brown by transmitted light. After standing for a short time, very tiny, colorless, highly refractive, strongly polarizing grains make their appearance ( $\text{CaCO}_3$ ?).

Strontium at first forms a granular precipitate; this is followed by small lichen-like disks or small mossy radiates, sometimes accompanied by tiny, drusy, fusiform crystals.

Barium yields well-defined, many-branched, moss-like dendritic clumps or coral-like branching masses of pink crystals. The color is very different from that obtained with  $\text{Mg}^{++}$  and the structure and size of the mossy or root-like radiates are very different from  $\text{Sr}^{++}$  (Fig. 90, page 135).

In materials containing several members of the alkaline earths the carbazide reaction fails for both calcium and strontium. But barium is readily detected in mixtures containing other members of Group II.

Magnesium can be identified in the presence of all other members of Group II, providing the analyst is well experienced with the test and tries a series of different dilutions.

Both magnesium and barium can ordinarily be detected simultaneously in the same test drop.

Zinc forms a gelatino-granular "amorphous" precipitate having an intense violet color. Cadmium yields a very similar precipitate but slightly more purple, and if the fragment method is used there is formed in addition a brown "amorphous" precipitate differentiating cadmium from zinc.

Manganous salts produce a reaction similar in all respects to that produced by cadmium.

Lead yields an "amorphous" granular pink precipitate, together with minute dendritic clumps.

Thallous salts produce "amorphous" violet precipitates, interspersed with minute rods, prisms, and crystalline aggregates, all black by transmitted light.

Mercuric salts produce beautiful deep-blue "amorphous" precipitates, soon followed by tiny disks, black by transmitted light. Mercurous nitrate yields a precipitate identical in appearance with that obtained with  $\text{Hg}^{++}$  *but no disks*.

Beryllium yields a slight precipitate, purple in color, and a vast number of symmetrical spherulites of very fine acicular crystals, brown by transmitted light. They polarize feebly and exhibit a black cross and polarization colors of the first order.

Aluminum yields a reaction substantially identical with that obtained with beryllium (Fig. 91, page 135).

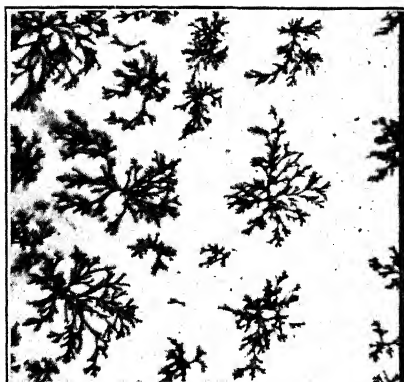


FIG. 90. Barium with Diphenylcarbazide. 200 $\times$ .

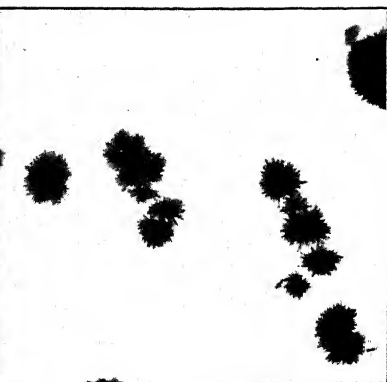


FIG. 91. Aluminum with Diphenylcarbazide. 100 $\times$ .



FIG. 92. Mercury with Ammonium Molybdate. 200 $\times$ .

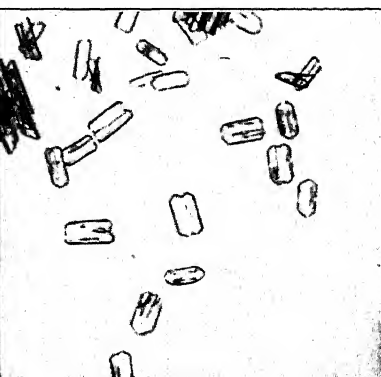


FIG. 93. Mercury with Ammonium Molybdate. 200 $\times$ .



FIG. 94. Aluminum with Ammonium Molybdate. 200 $\times$ .

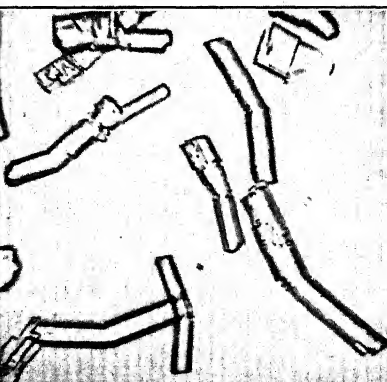


FIG. 95. Boric Acid Precipitated from Borates by Conc. Hydrochloric Acid. 150 $\times$ .

In materials containing Mg and Be or Mg and Al both metals can be detected simultaneously. Al or Be can be detected in the presence of Ca, Sr, and Ba.

Ga, In, Fe, Cr, Cu, Co, Ni, all produce deeply colored "amorphous" precipitates but without sufficiently characteristic differences in color to permit differentiation. Since the colors are different shades of violet and purple, any one of them may mask the reaction for magnesium unless magnesium is the predominating ion.

There appears to be a distinct advantage in the addition of the solid unknown to the reagent drop when dealing with mixtures containing salts of quite different solubilities, for under these conditions there can be formed a series of zones of precipitates of different colors or different crystalline precipitates.

#### D. By Means of Potassium Antimonate — $K[Sb(OH)_6]$ .

Perform the test as suggested under Sodium, page 90. Magnesium antimonate under these conditions should separate in hexagonal plates and tablets. It has been shown,<sup>29</sup> however, that monoclinic crystals or an "amorphous" precipitate may result under certain equilibrium conditions. If the test drop is highly concentrated in magnesium ions, there will usually be obtained a mixed precipitate consisting of "amorphous" matter and both monoclinic and hexagonal crystals. In properly dilute solutions, hexagons alone are obtained (Fig. 40, page 61).

According to Pauling the magnesium salt which separates has the formula  $Mg(H_2O)_6 \cdot [Sb(OH)_6]$ .

### DETECTION OF ZINC AND CADMIUM<sup>30</sup>

#### A. By Means of Potassium Mercuric Thiocyanate — $K_2Hg(SCN)_4$ .

*Compounds Formed* —  $ZnHg(SCN)_4$

$CdHg(SCN)_4$ .

Apply the reagent by Method I, page 31, or by Method II, page 33.

The test appears to be slightly more sensitive when made by Method II, but much better preparations are obtained by Method I.

The reagent drop should be concentrated, but the test drop very dilute and may contain a trace of free nitric acid.

Although traces of strong acids do not appear to have a deleterious

<sup>29</sup> Obajdin: *Chem. Abstr.* 16, 3597 (1922).

<sup>30</sup> For a comprehensive Bibliography on Cadmium, see *Mikrochemie* 19, 147 (1935).

Benedetti-Pichler and Spikes: *Mikrochemie* 15, 271 (1934), have shown that analogous compounds are formed when selenium replaces sulphur in the thiocyanate ions.

effect upon the reactions obtainable with  $\text{K}_2\text{Hg}(\text{SCN})_4$ , it is always a wise precaution to add a little  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  or  $\text{NaC}_2\text{H}_3\text{O}_2$ . A small fragment may be added and the test drop warmed and stirred until the salt has dissolved; a slight excess of alkali acetate is favorable to the production of typical crystals of the double thiocyanates of both zinc and cadmium. In the tests for the presence of  $\text{Cu}^{++}$ ,  $\text{Co}^{++}$ , and  $\text{Ni}^{++}$ , as well as  $\text{Zn}^{++}$  and  $\text{Cd}^{++}$ , however, consistently better crystals appear to be obtained when all the free mineral acid has not been buffered by the use of an excess of alkali acetate.

Zinc yields an almost instantaneous precipitation of pure white (colorless) feathery crosses and branching feathery aggregates which appear black by transmitted light (Fig. 96, page 139). From very dilute solutions this salt —  $\text{Zn}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2$  — crystallizes in right-angled orthorhombic prisms or square tablets and fourlings, but under the conditions which usually obtain in testing upon an object slide skeleton and dendritic crystals predominate and prismatic crystals are seldom obtained; the dendrites are, however, peculiar to  $\text{Zn}^{++}$ , and furnish one of the best, most sensitive, and most reliable micro tests for  $\text{Zn}^{++}$  at our disposal.

The cadmium salt  $\text{Cd}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2$  separates more slowly in brilliant, colorless, orthorhombic prisms usually several times as long as broad, one end usually pyramidal, the other beveled or truncated (probably sphenoidal or bisphenoidal); an almost constant peculiarity is the presence of cavities near each end of the prisms (Fig. 97, page 139). As in the case of  $\text{Zn}^{++}$ , the habit of the  $\text{Cd}^{++}$  double thiocyanate is peculiar to the element and thus affords a most valuable test. The prisms are single, and are rarely grouped or in aggregates, unless formed in concentrated solutions.

Copper forms the salt  $\text{Cu}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2 \cdot \text{H}_2\text{O}$ , greenish yellow in color, in mossy dendrites and in fusiform or boat-shaped crystals; radiating groups of pointed prismatic crystals are also abundantly formed (Fig. 100, page 139). The only other element giving a reaction in any way resembling that of copper is gold.

When potassium mercuric thiocyanate is added by Method II to a test drop containing chloroauric acid (even if the latter is moderately acid with  $\text{HCl}$  or  $\text{HNO}_3$ ), the reagent fragments are immediately covered with a coating of exceedingly fine needles having an orange-red color. These needles grow outward as the reagent slowly dissolves and eventually develop into masses of mossy dendrites (Fig. 101, page 139). Just outside this zone of dendrites there is usually formed an interrupted zone of white "amorphous" material (aurous), and out beyond this zone of white precipitate metallic gold may sometimes be precipitated

After a short time the mossy dendrites attain considerable dimensions but do not develop into the long acicular prisms, nor the boat-shaped nor fusiform crystals obtained with copper, nor do they exhibit the greenish yellow color so characteristic of copper. The reddish color of the gold compound is more pronounced if examined with crossed nicols. When this is done there can be no difficulty in differentiating the two compounds. (See Gold, Test B, page 305.) The composition of the reaction products obtained with gold has not yet been definitely established.

The cobalt salt  $\text{Co(SCN)}_2 \cdot \text{Hg(SCN)}_2$  is quite soluble and therefore separates only as the concentration rises through evaporation. It forms beautiful, deep-blue pleochroic ("cobalt blue"), star-like groups and radiating masses of imperfectly developed orthorhombic prisms (Fig. 99, page 139). In the presence of much cobalt small amounts of zinc will usually escape detection. The qualification "usually" is made because, under certain conditions of relative concentrations of reagent and test drop, the much less soluble zinc salt may separate during a very short interval of time before the bulk of the cobalt salt is precipitated; but the analyst may not be studying the preparation at this precise moment. It is therefore essential that the cobalt be removed before testing for the presence of very small percentages of zinc or cadmium. (See Cobalt, Method A, page 269.)<sup>31</sup>

It has been pointed out by Short<sup>32</sup> that, under certain conditions of concentration of cobalt ions, prisms and radiates are not formed but only spherulites, and that  $\text{Ni}^{++}$  and  $\text{Fe}^{++}$  present in the test drop may have a similar effect.

It is well to bear in mind that the addition of the reagent to a test drop containing  $\text{Hg}^{++}$  will be followed by a precipitation of  $\text{Hg(SCN)}_2$  which may destroy the reagent or mask a reaction.

In the presence of even a very small amount of cadmium <sup>+</sup>the zinc salt loses its feathery character, though a few large crosses and star-like dendrites may still be formed; more cadmium forces the zinc salt into arrow-head forms (Fig. 98, page 139; still more cadmium gives rise to elongated arrowheads, slender prisms of irregular outline or thin plates; these pass by very gradual transitions into the typical prisms of the pure cadmium salt. A small amount of zinc in a large amount of cadmium may thus escape detection; but a small amount of cadmium in a large amount of zinc is readily discovered.

Copper usually separates before the zinc salt, but, when present in

<sup>31</sup> For a comprehensive discussion of this salt, see Augusti: *Gazz. chim. Ital.* 64, 33 (1934); Korenman: *Zeit. anal. Chem.* 95, 44 (1933).

<sup>32</sup> *U. S. Geol. Surv. Bull.* 825, 135-137 (1931).





FIG. 96. Zinc with Potassium Mercuric Thiocyanate. 100X.



FIG. 97. Cadmium with Potassium Mercuric Thiocyanate. 100X.



FIG. 98. Zinc + Cadmium with Potassium Mercuric Thiocyanate. 100X.

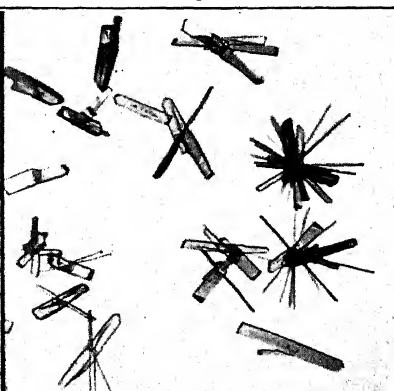


FIG. 99. Cobalt with Potassium Mercuric Thiocyanate. 100X.

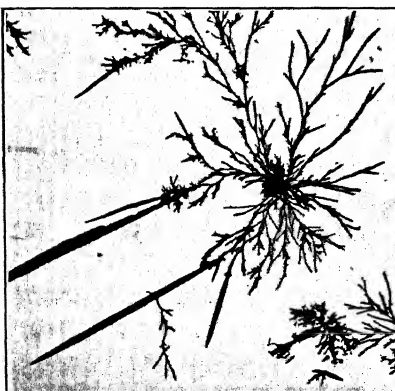


FIG. 100. Copper with Potassium Mercuric Thiocyanate. 100X.



FIG. 101. Gold with Potassium Mercuric Thiocyanate. 100X.

traces only, it colors the crystals of the zinc and the cadmium double thiocyanates without in any way changing their habit. A trace of copper gives a lavender or violet tint; more copper colors the crystals chocolate, brownish, or even black, and drusy spherulites, almost opaque, may appear. In dilute solutions in which the  $\text{Zn}^{++}$  is in decided excess of  $\text{Cu}^{++}$ , no crystals of copper mercury thiocyanate are apt to be seen but only crystals of a solid solution of the  $\text{Cu}^{++}$  salt in the  $\text{Zn}^{++}$  or  $\text{Cd}^{++}$  salt. But if the  $\text{Cu}^{++}$  is in excess of the  $\text{Zn}^{++}$ , the zinc double salt separates first deeply colored and later the yellow copper salt appears. This is true in dilute solutions only; in more concentrated solutions the copper salt may be the first to appear. The addition of a very little copper acetate to a test drop suspected of containing traces of zinc or cadmium increases the probabilities or detecting these cations.

The cobalt double thiocyanate entering into solid solution in the zinc or cadmium double salts colors them very faintly blue when only a trace of cobalt is present; the intensity of the coloration increases with the rise in  $\text{Co}^{++}$  concentration until the tint is so dark as to render the crystals almost black. With small amounts of cobalt the feathery zinc mercury thiocyanate crystals are merely tinted blue and the crystal form remains unchanged, but with a rise in the  $\text{Co}^{++}$  concentration, the zinc salt becomes less and less feathery until the crystals become a solid solution of the zinc salt in the prismatic crystals of cobalt mercury thiocyanate. Owing to the much greater solubility of the cobalt salt than that of the copper salt, the addition of cobalt to a test drop in which zinc or cadmium is sought is of much less value than the addition of  $\text{Cu}^{++}$ . With much cobalt and little cadmium only the cobalt forms are obtained.

The presence of a high percentage of both  $\text{Cu}^{++}$  and  $\text{Co}^{++}$  in solutions containing  $\text{Zn}^{++}$  or  $\text{Cd}^{++}$  gives rise to crystals of very peculiar colors and forms which are very different from those obtained when either  $\text{Co}^{++}$  or  $\text{Cu}^{++}$  alone is present with the  $\text{Zn}^{++}$  or  $\text{Cd}^{++}$ .

Nickel gives no reaction unless the test drop is very highly concentrated with respect to  $\text{Ni}^{++}$ . There will then be obtained tiny yellowish disks and spherocrystals which are almost colorless; the thicker masses of the infinitely fine radiating needles appear brownish by transmitted light (structural color).

Manganous salts under favorable conditions yield colorless, irregular, slender prisms, singly and in masses, somewhat resembling badly formed crystals of the cadmium salt, but readily differentiated because the clear-cut, straight-edged prisms terminating in beveled, truncated, or pyramidal faces are not formed (Fig. 103, page 143). From its

habit and behavior it is probable that the salt has the formula  $\text{Mn}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2$  and is isomorphous with the  $\text{Zn}^{++}$ ,  $\text{Cd}^{++}$ , and  $\text{Co}^{++}$  salts. A trace of  $\text{H}_2\text{SO}_4$  favors the separation of the  $\text{Mn}^{++}$  salt. The best results are obtained when manganese is present as acetate and the drop contains a little alkali acetate.

Lead is precipitated in granular form or as prismatic-monoclinic crystals from concentrated solutions of  $\text{Pb}(\text{NO}_3)_2$ , and may interfere with the test for Zn and Cd. Lead should, therefore, be removed by treating with  $\text{H}_2\text{SO}_4$  before testing with  $\text{K}_2\text{Hg}(\text{SCN})_4$ . But if the test drop contains much  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , there may be formed radiating clusters of colorless slender tapering prisms, in outline resembling the blue  $\text{Co}^{++}$  salt (Fig. 102, page 143).

Silver yields a fine granular precipitate soon developing into tiny, thin, slender prisms with square or oblique ends, at times somewhat resembling the cadmium salt but not to be confused with the latter since the crystals of the silver salt always remain very small. Much silver masks the zinc and the cadmium reactions and must first be removed by precipitation with  $\text{HCl}$ .

Ferrous salts yield no visible reaction in dilute solutions and do not under these conditions interfere with the detection of zinc or cadmium. If the test drop is highly concentrated in ferrous ions and a fragment of potassium mercuric thiocyanate is added thereto, faintly lemon-yellow, stout, transparent, strongly contoured prisms with square or truncated ends are formed in radiating clumps. These prisms exhibit parallel extinction and colors of the first and second orders. As the preparation passes almost to dryness, masses of mossy dendrites or spherulites may appear.

Ferric salts yield at once the blood-red color of  $\text{Fe}(\text{SCN})_3$ . If more than a mere pink color is produced, the reaction for all the cations mentioned above will be masked either because of the intense color of the solution or because the crystals which separate take up the ferric salt in solid solution and become reddish, reddish-brown, or almost black. This is eventually accompanied by a remarkable change into masses of curving, branching, filiform crystals. This latter phenomenon is accentuated if  $(\text{NH}_4)\text{C}_2\text{H}_3\text{O}_2$  or  $\text{NaC}_2\text{H}_3\text{O}_2$  are present in the drop which may happen if a marked excess of either of these reagents has been used to mitigate the action of free mineral acids.

No cations other than those mentioned above yield crystals with  $\text{K}_2\text{Hg}(\text{SCN})_4$  under the conditions prescribed above, but the descriptions of the solid phases which separate apply only to those cases where the *single* cation is present. In mixtures of these cations a variety of phenomena may be obtained.

The double thiocyanate reaction (first proposed by Behrens) we have found to be the most useful, satisfactory, and generally dependable test that has yet been found for the microscopical identification of  $\text{Zn}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Cu}^{++}$ , and  $\text{Co}^{++}$ . The salt  $\text{K}_2\text{Hg}(\text{SCN})_4$ <sup>33</sup> appears to be a more reliable reagent than a solution prepared by adding  $\text{NH}_4\text{SCN}$  to a solution of  $\text{HgCl}_2$  until the precipitate first formed is just redissolved. It is also a more satisfactory reagent than either the ammonium or the sodium double salt since it is stable and not hygroscopic. Although it was found that the sodium salt yields a slightly more sensitive reaction than does the potassium salt, this slight increase is outweighed by its deliquescent character and its lack of stability on keeping. When dealing with mixtures containing members of the platinum group, however, the sodium salt<sup>34</sup> should be employed in order to avoid the precipitation of potassium.

In a mixture containing two or more elements and in which the percentage of either zinc, cadmium, copper, or cobalt is greatly in excess of other elements, the presence of the predominating cation governs the type of crystals formed, and the cations in small amount may be completely overlooked by the analyst unless he is on his guard.

Moreover, in most mixtures containing these elements in almost equal amounts the crystal forms (and colors) are usually completely changed, and are apt to prove at times extremely puzzling. Changes in the appearance of the crystals may be brought about by elements other than those listed above. Such changes, however, serve to indicate at once that more than a simple cation is present in the test drop.

Iodide and other ions yielding precipitates with  $\text{Hg}^{++}$  interfere with the reactions by destroying the reagent.

When much nickel and very little cobalt are present, the reaction for cobalt is apt to fail.

For complicated cases such as those just referred to there can be no "guide" outlined, but for simple mixtures the following tabulation may prove useful.

The material is dissolved in concentrated  $\text{HNO}_3$  and evaporated to dryness to remove any tin and to remove iodide and other anions which might destroy the reagent. The residue is treated with  $\text{HNO}_3$  and again evaporated. If a white residue (metastannic acid) is obtained, extract with dilute  $\text{HNO}_3$ , decanting or filtering. Evaporate the solution carefully to dryness at a low temperature, add water — if a precipitate or turbidity results ( $\text{Bi}$ ,  $\text{Sb}$ ), decant or filter. If lead or silver

<sup>33</sup> Chipman, Ruth E., Unpublished Thesis, Cornell University, 1917. For the preparation of  $\text{K}_2\text{Hg}(\text{SCN})_4$ , see Appendix, page 421.

<sup>34</sup> Strebinger and Holze: *Mikrochemie* 8, 264 (1930).

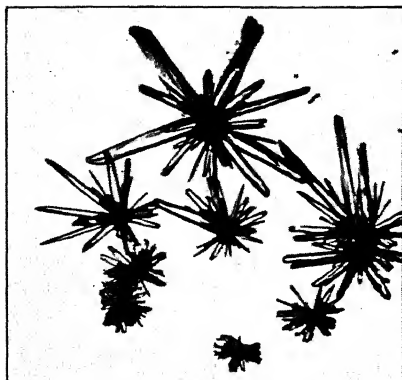


FIG. 102. Lead with Potassium Mercuric Thiocyanate. 100 $\times$ .

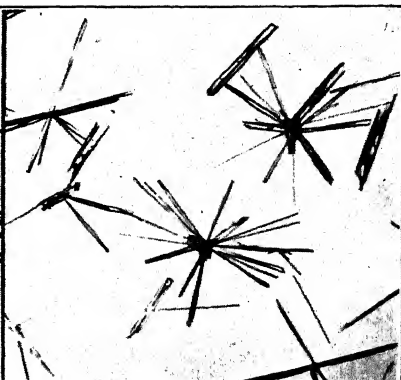


FIG. 103. Manganese ( $Mn^{++}$ ) with Potassium Mercuric Thiocyanate. 100 $\times$ .

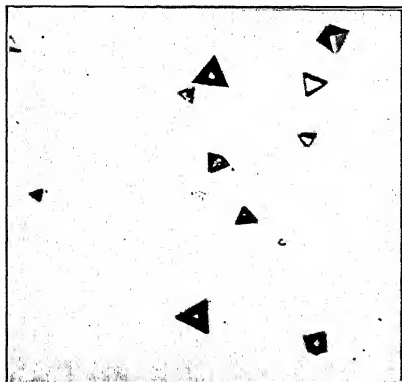


FIG. 104. Zinc with Sodium Bicarbonate. 200 $\times$ .

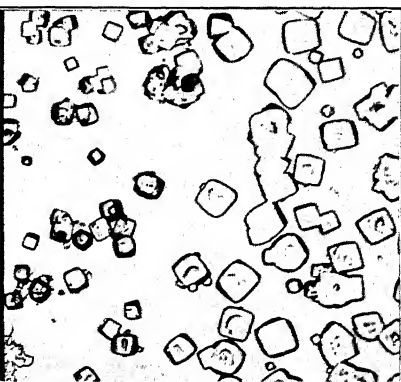


FIG. 105. Zinc with Sodium Nitroprusside. 200 $\times$ .

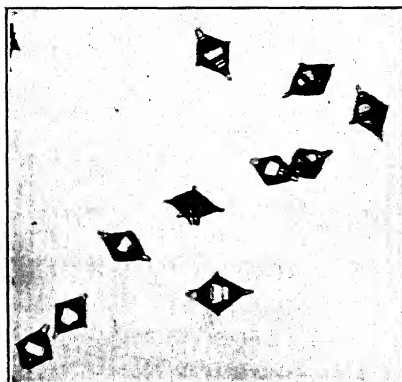


FIG. 106. Cadmium with Cesium Chloride. 200 $\times$ .

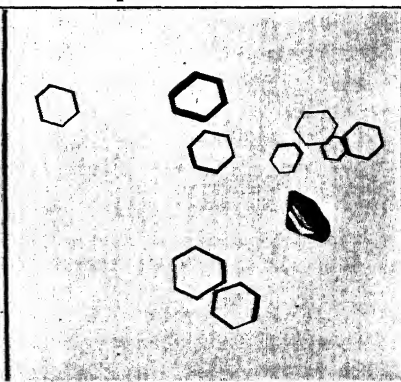


FIG. 107. Cadmium with Cesium Chloride. 100 $\times$ .

is probably present, add HCl to the filtrate and filter. To the filtrate add  $(\text{NH}_4)\text{C}_2\text{H}_3\text{O}_2$  and  $\text{K}_2\text{Hg}(\text{SCN})_4$  as directed on page 136.

There results:

- A. *A white or faintly yellow or brown dense precipitate without any definite crystal form:*  
 Au or Cd in too concentrated solution.  
 Pb, Ag, Mn, Ni, Hg,  $\text{Fe}^{++}$ .
- B. *Make a very dilute solution and test again:*
  - a. Feathery pure white (black by transmitted light) crosses, X's, and irregular feathery dendrites: Zn.
  - b. Colorless, clean-cut, straight-edged prisms, with pyramidal or beveled ends: Cd.
  - c. White, granular precipitate or tiny skeleton crystals and plates: Pb. Confirm by HCl or KI.
  - d. White and colorless arrowheads or irregular crystallites: Zn, and any or all of the following: Cd, Ni, Mn,  $\text{Fe}^{++}$ .
- C. *The Zn crystallites are blue:* Zn and Co.  
 The Cd prisms are blue: Cd and Co.  
 Blue crystallites and arrowheads: Zn, Cd, and Co, (Fe, Ni).  
 Dark-blue, tapering, radiating prisms: Co, and any or all of the following: Zn, Cd, Ni, Mn.
- D. *The Zn crystallites are lavender, brown, or black:* Zn and Cu.  
 The Cd prisms are lavender or brown: Cd and Cu.  
 Irregular crystallites, brownish blue or bluish green: Zn (and possibly Cd, Ni, Mn) with Cu and Co.
- E. *Lemon-yellow, mossy dendrites and elliptical plates or fusiform crystals:* Cu.
- F. *Golden, mossy dendrites with a metallic luster; no fusiform prisms or plates:* Au. (See Gold, page 305.)
- G. *The solution is colored pink or red:* Fe. (Or red, brown or black crystals in a red solution.)

For further information relative to variations from normal in crystal forms and colors due to mixtures of metals, see Whitmore and Schneider: *Mikrochemie* 8, 293 (1930); Short: *op. cit.*, p. 129.

### Experiments.

(a) Apply the thiocyanate reagent, in the manner indicated, to solutions of pure Zn salts of different degrees of concentration.

(b) Try in turn pure salts of Cd, Cu, Co, Ni, Ag, and Pb.

(c) To a Zn solution add a very little Cd and test. Repeat the experiment, using more Cd.

(d) In like manner try mixtures of Zn and Cu; Zn and Co; Zn and Fe; Zn and Mg; Zn and Al; Zn and Pb; Zn and Ag.

(e) Then try more complex mixtures, as, for example: Zn, Cd, and Cu; Zn, Cd, and Co; Au, Cu, and Co; etc.

In each case prepare several slides under different conditions and note well the changes in the appearance in the crystals which separate.

### B. By Means of Sodium Bicarbonate — $\text{HNaCO}_3$ .

*Compound Formed* —  $3 \text{Na}_2\text{CO}_3 \cdot 8 \text{ZnCO}_3 \cdot 8 \text{H}_2\text{O}$ .

This sodium-zinc salt can be obtained by several different procedures: addition of a saturated solution of  $\text{HNaCO}_3$  to a neutral test drop, or to a drop made ammoniacal with  $\text{NH}_4\text{OH}$ , or to a drop made strongly alkaline with  $\text{NaOH}$ . All three methods give excellent results with pure salts of zinc, but none are wholly dependable when dealing with mixtures such as alloys containing zinc. In the presence of cadmium the procedure using  $\text{NaOH}$  is alone reliable.

The salt  $3 \text{Na}_2\text{CO}_3 \cdot 8 \text{ZnCO}_3 \cdot 8 \text{H}_2\text{O}$  separates slowly in the form of small, colorless, triangular plates and isotropic tetrahedra (Fig. 104, page 143). Three-armed and five-armed dendrites are also formed, the arms of which generally terminate in tetrahedra. Short stout prisms with pointed ends are also formed. The tetrahedra are constant and peculiar to zinc; no other element yields similar crystals with  $\text{HNaCO}_3$ .

There is first precipitated by the reagent a fine formless precipitate consisting of a basic carbonate of zinc; this salt in the presence of an *excess* of alkali carbonate is slowly transformed into the characteristic sodium zinc carbonate. This latter salt adheres firmly to the object slide, permitting easy decantation and washing. It can then be dissolved and subjected to other confirmatory tests.

Since a large number of cations are precipitable by alkali carbonates, forming bulky compounds, the reaction for zinc is often completely masked, or, if not, the habit of the sodium zinc carbonate may be so modified that the test becomes unreliable. To avoid these difficulties Schoorl<sup>35</sup> has suggested the following procedure. To the dilute solution to be tested, sufficient  $\text{NaOH}$  is added to convert the precipitated zinc hydroxide into sodium zincate which passes into solution. To insure solution add a slight excess of  $\text{NaOH}$  and stir thoroughly. Decant, centrifuge, or filter (through asbestos). Then add to the filtrate  $\text{HNaCO}_3$  in a *very fine* powder, in slight excess, so that some of the solid alkali carbonate remains undissolved in suspension. Thorough stirring is essential, but care must be used to avoid rubbing the glass slide during the stirring or there will result an immediate precipitation of sub-microscopic crystals upon the surface of the glass. These tiny crystals rarely develop into recognizable forms.

<sup>35</sup> *Beiträge z. mikrochem. Anal.*, p. 105.

After the stirring the preparation should be set aside for a few minutes in order to allow time for the growth of typical crystals.

If the solution is too dilute, no crystals will appear until sufficient evaporation has taken place to permit the separation of the double salt. Concentration of the test drop by heating after the addition of the reagent is not permissible.

If Schoorl's method is followed, cadmium does not interfere with the test for zinc since a soluble carbonate is not readily formed.

In mixtures of cadmium and zinc, if no separation of the zinc is attempted but the reagent  $\text{HNaCO}_3$  added at once, a cadmium double carbonate is precipitated, with or before the zinc, in granular form masking the zinc reaction.

Behrens<sup>36</sup> has shown that it is possible to differentiate between zinc and cadmium by adding an excess of  $\text{HNaCO}_3$  to an ammoniacal test drop. The cadmium double carbonate separates first, and if the supernatant liquor is decanted before the zinc salt separates, typical tetrahedra can be found in the decanted solution after it has stood for a short time. Satisfactory results are obtainable with comparatively simple mixtures only, since the alkaline earths, members of Group VIII, etc., are also precipitated with the zinc and cadmium.

#### Experiments.

(a) Try precipitating Zn in neutral and in ammoniacal solutions. Try decantation from the precipitate.

(b) Test mixtures of Zn and Cd, first in neutral and then in ammoniacal solutions.

(c) Experiment with Zn in the presence of the interfering elements noted above.

#### C. By Means of Oxalic Acid — $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ .

*Compounds Formed* —  $\text{ZnC}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$

$\text{CdC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$ .

The reagent is applied by Method I to the neutral or slightly acid test drop, which should be moderately concentrated.

$\text{ZnC}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$  separates as small double spherulites or as tiny pseudo-octahedra, singly or united end to end in two's; thin rhombs are also formed (Fig. 84, page 119). It is rare that a preparation can be obtained in which well-formed, clear-cut crystals can be found. The usual habit is that of grains with rounded angles or disks, appearing as if the crystals had begun to dissolve.

<sup>36</sup> Behrens: *Anleitung*, 2 Auf., p. 52. Behrens-Kley: *Mikrochem. Anal.*, p. 70. This method requires skill and experience, and reliable results are possible under the most favorable conditions only.



Under a low power the crystals of zinc oxalate often bear a striking resemblance to the imperfectly developed oxalates of calcium and strontium. It is therefore unwise to place dependence upon an oxalate precipitate alone, if zinc is being sought.

Cadmium, on the other hand, gives clear, colorless, well-developed monoclinic prisms and tabular crystals of the salt  $\text{CdC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$  (Fig. 85, page 119). The prisms are usually thin, long, and narrow, with square or more often obliquely truncated ends, the acute angle being about  $60^\circ$ . The extinction angle (with long edge) is  $24^\circ$  (Haushofer). The prisms occur singly in X's and in irregular radiates consisting of lath-shaped crystals of greatly varying sizes. The tabular crystals are, in outline, rectangular or unsymmetrical, elongated hexagons. From very concentrated solutions, octahedral crystals are obtained in addition to the prisms and plates.

The typical prismatic crystals of  $\text{CdC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$  are obtainable only when dealing with almost pure salts of cadmium. Very small percentages of zinc do not seriously interfere; but, when the ratio of zinc to cadmium exceeds 1 : 10, the prisms are shortened and as the proportion of zinc increases the precipitate takes on the habit of zinc oxalate and no indication of the presence of cadmium is obtained.

Manganese gives  $\text{MnC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$ , which separates in radiates closely resembling those of the cadmium salt, but more regular and star-like (Fig. 89, page 119). Some of the prisms have pointed, some square, and some obliquely truncated ends. The acute angle of truncation, although less than that in the cadmium salt, is too close to it to be useful as a means of differentiation.  $\text{MnC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$  can be distinguished from  $\text{CdC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$  since it is very strongly birefringent, exhibits brilliant polarization colors, and extinguishes *parallel* to the elongation of the prisms.

Mixtures of zinc and cadmium, zinc and manganese, cadmium and manganese, give mixed crystals whose appearance varies with the relative proportion of these elements. In most cases the appearance is such that the experienced analyst can form a fairly reliable opinion as to the nature of the mixture with which he is dealing.

Free mineral acids are objectionable.

The test may be masked by the presence of salts of silver, lead, mercury, tin, copper, and trivalent metals.

More than traces of magnesium usually seriously modify the habit of the oxalates of both zinc and cadmium.

For data relative to oxalates which may separate when oxalic acid or alkali oxalates are used as reagents, see page 120.

Alkali oxalates may be substituted for oxalic acid, thus slightly

increasing the delicacy of the test but not improving the character of the crystals which separate.

**D. By Means of Sodium Nitroprusside<sup>37</sup>— $\text{Na}_2\text{NOFe}(\text{CN})_5 \cdot 2 \text{H}_2\text{O}$ .**

*Compound Formed* —  $\text{Zn} \cdot \text{NOFe}(\text{CN})_5 \cdot \text{H}_2\text{O} (?)$

The best results are obtained when the reagent is applied by Method I to a neutral test drop of moderate concentration. A small amount of free mineral acid is in no way objectionable, but much acid causes a complete change in the habit of the crystals.

Zinc forms a nitroprusside of low solubility and is precipitated at once in spherical grains, botryoidal masses, and in tiny circular disks having a faintly brownish color but usually so thin as to appear to be colorless. On long standing the spherical grains develop a large number of faces, and grains can be found which show what appear to be faces of the cube, octahedron, and dodecahedron and combinations of these (Fig. 105, page 143). The crystals are isotropic. The formula of the compound has not been definitely established.

In distinctly acid solutions there may be formed rectangular prisms, square plates, and fusiform rods.

Heat hastens the reaction but does not produce better-formed crystals.

Cadmium yields tiny drusy globulites, octahedra with rough, corrugated, or bristling faces, and drusy aggregates. The crystals are strongly birefringent, and the larger ones exhibit brilliant polarization colors. Their behavior toward polarized light provides a means of easily differentiating between cadmium and zinc.  $\curvearrowright$

Mixtures of cadmium and zinc yield rough globulites not to be distinguished from the first-formed drusy globulites of cadmium. Such mixed crystals are generally anisotropic.

$\text{Mn}^{++}$  forms a nitroprusside that cannot be distinguished from that of  $\text{Zn}^{++}$ ; both have the same habit, are of like size, and both are isotropic.

With  $\text{Cu}^{++}$  there is first formed an "amorphous" pale-blue precipitate in which later there may develop star-like skeleton crystals. Mixtures of  $\text{Cu}^{++}$  and  $\text{Zn}^{++}$  yield the "amorphous" blue precipitate and the spherical grains and disks of  $\text{Zn}^{++}$ , but the zinc salt in this case resembles the cadmium salt more closely than the typical forms of zinc, but are readily differentiated since they are isotropic.

$\text{Ni}^{++}$  forms a flocculent light-green precipitate and  $\text{Co}^{++}$  a similar pink one. Iron (unless very concentrated) gives no reaction unless the preparation is heated and then a yellow deposit only.

Mercurous salts are precipitated as a yellowish, gelatinous mass.

$\text{Hg}^{++}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{++}$ ,  $\text{Sn}^{++}$ ,  $\text{Sn}^{++++}$ ,  $\text{Sb}^{+++}$ ,  $\text{Bi}^{+++}$ ,  $\text{Al}^{+++}$ ,  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Ba}^{++}$  give no precipitates and yield no crystalline salts even in high concentrations or on evaporation almost to dryness.

When using sodium nitroprusside as a reagent, if no reaction is obtained on the first test, repeat using a much more concentrated test drop. Then heat the preparation. A precipitate indicates the presence of  $\text{Zn}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Mn}^{++}$ , or  $\text{Cu}^{++}$ . If no precipitate is obtained, these elements are absent.

<sup>37</sup> Bradley: *Amer. Jour. Sci.* 22, 326 (1906). This test was developed for the identification of zinc in shellfish, and according to its originator is the only specific micro test for zinc in material of this sort.

**E. By Means of Rubidium Chloride or Cesium Chloride.<sup>38</sup>**

*Compounds Formed* —  $4 \text{ RbCl} \cdot \text{CdCl}_2$   
 $4 \text{ CsCl} \cdot \text{CdCl}_2$ .

A. When  $\text{RbCl}$  is employed as reagent it should be added by Method III, page 35. This method or that of covering the dry residue with a drop of the reagent (Schoorl) is essential if characteristic crystals are to be obtained. Of the two methods the authors prefer the first or "streak" method. The reagent drop should be almost saturated.

$4 \text{ RbCl} \cdot \text{CdCl}_2$  crystallizes in a variety of forms in which colorless, highly refractive, well-developed rhombohedral tablets predominate (Fig. 108, page 151). Short, stout, hexagonal prisms with pyramidal or blunt ends are also formed. These prisms are weakly birefringent with parallel extinction. Curious barrel-shaped aggregates, strongly birefringent, are almost always present (Fig. 109, page 151). The rhombohedral tablets have their angles so near  $90^\circ$  and so many of them lie in positions showing low birefringence that they are not readily distinguished from plates of  $\text{RbCl}$ . In many preparations six-sided plates and tablets separate in large numbers. In such crystals two of the opposite and parallel sides are much shorter than the other four. Symmetrical hexagons are rare (distinction from  $\text{Sb}^{+++}$  and  $\text{Bi}^{+++}$ ). These six-sided tablets, if carefully focused, cannot be confused with such cubes of  $\text{RbCl}$  as lie in a position yielding a six-sided image in the microscope.

Since we are dealing with a dry residue, prismatic crystals are almost always present. To avoid confusion the search for characteristic crystals of the double salts should be confined to a zone well inside the reagent channel.  $\text{CdCl}_2 \cdot 2\frac{1}{2} \text{ H}_2\text{O}$  forms monoclinic lath-shaped crystals and long thin prisms with square ends, singly, in aggregates, or in sheaf-like bundles. They are strongly birefringent and most of them show parallel extinction.

Characteristic crystals of  $4 \text{ RbCl} \cdot \text{CdCl}_2$  are seldom obtainable from cadmium salts other than the chloride. Although the nitrate can be made to yield a satisfactory test, it is always wise to evaporate repeatedly with concentrated  $\text{HCl}$  if the material to be analyzed contains nitrates or has been brought into solution with  $\text{HNO}_3$  or with aqua regia. If cadmium is present as a sulphate, the test is unreliable or fails.

The rubidium zinc chloride is so very soluble that it does not separate until the channel of the reagent passes to dryness, and even then well-formed crystals are not likely to be obtained.

<sup>38</sup> Rimbach: *Ber.* 35, 1306 (1902).

Schoorl: *Beiträge z. mikrochem. Anal.*, p. 70.

The usefulness of the rubidium chloride test for cadmium is very limited because  $\text{RbCl}$  forms double chlorides with the chlorides of a large number of elements, many of which are to be found associated with cadmium. Some of these double chlorides are of about the same solubilities as the rubidium cadmium salt. Moreover,  $\text{RbCl}$  is a reagent rarely used and the analyst is seldom familiar with its many double salts.

*B.* Considered from all points of view,  $\text{CsCl}$  appears to be a more useful reagent than  $\text{RbCl}$  for the identification of cadmium, but its successful use is more closely dependent upon carefully controlled conditions than is the case with  $\text{RbCl}$ .

The reagent is best applied by Method I, page 31. The test drop should be moderately concentrated (see page 153) and free from an excess of acid. The cadmium must be present as chloride, not as sulphate. The reagent drop must be an almost saturated solution of  $\text{CsCl}$ .

The compound formed is probably  $4 \text{CsCl} \cdot \text{CdCl}_2$ . It separates first in tiny, highly refractive grains or tiny crystals which appear to be octahedra but which will be found on careful focusing to be hexagonal bipyramidal twins (distinction from  $\text{Cs}_2\text{SnCl}_6$ ). (See Fig. 106, page 143). These twins consist of hexagonal pyramids united at their basal planes; many of them soon elongate into what appear to be stout bipyramidal prisms with a prominent swelling midway in their lengths and with many marked cross striations; they are very characteristic and are specific for cadmium. Single pyramids with their basal planes in contact with the glass slide develop into isotropic hexagonal plates and tablets (Fig. 107, page 143).

No separation of crystals is obtained with zinc until the preparation has stood for some time and evaporation has carried the test drop nearly to dryness (*i.e.*, to complete saturation with respect to the cesium zinc chloride). Under these conditions, if much zinc is present, large, colorless, imperfectly developed prisms and tablets of the cesium zinc salt may appear. These crystals have parallel extinction, are strongly birefringent, and show brilliant polarization colors. The reaction is of no value for the identification of zinc, for the crystals of the double salt are not characteristic and their solubility is too high.

Mixtures of cadmium and zinc gives the typical bipyramidal or rhomb-shaped twins of cesium cadmium chloride unless the zinc is greatly in excess of the cadmium.

Since cesium chloride forms double chlorides of low solubilities with many elements, there are many possibilities of interferences; the analyst must therefore be on his guard lest he misinterpret a reaction.

$\text{CsCl}$  applied to the test drop by Method III as is practiced with  $\text{RbCl}$

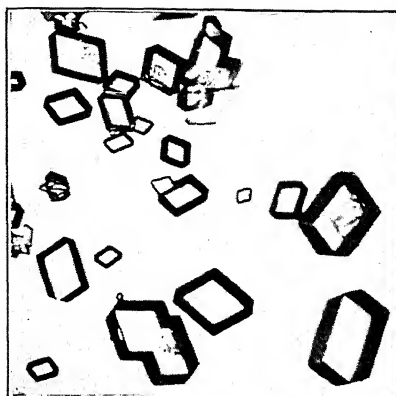


FIG. 108. Cadmium with Rubidium Chloride. 150X.



FIG. 109. Cadmium with Rubidium Chloride. 200X.



FIG. 110. Mercury ( $\text{Hg}^+$ ) with Potassium Bichromate. 100X.

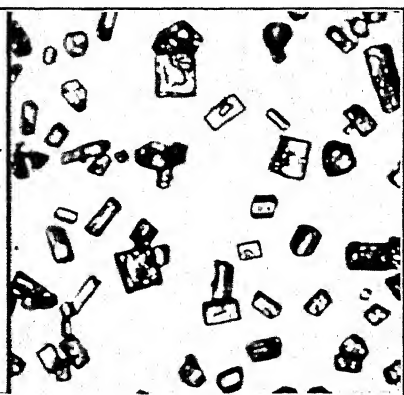


FIG. 111. Mercury ( $\text{Hg}^{++}$ ) with Potassium Iodide. 300X.

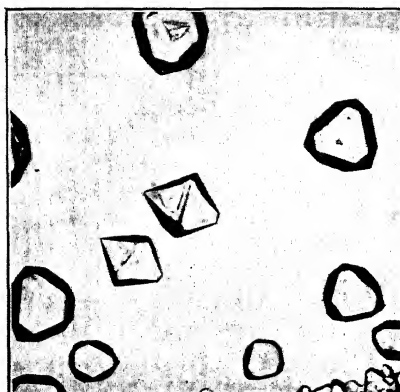


FIG. 112. Aluminum with Cesium Sulphate. 100X.

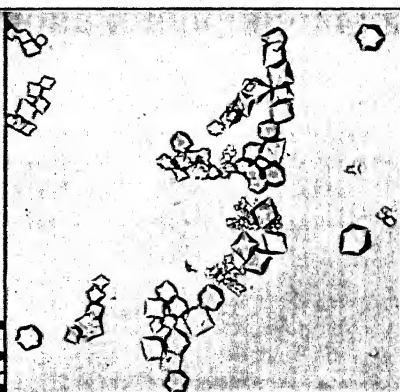


FIG. 113. Aluminum with Ammonium Fluoride. 200X.

is prone to yield unsatisfactory results because of the immediate formation of a granular precipitate or of hexagonal plates and tablets to the exclusion of the more typical bipyramidal twins.

Cesium chloride readily forms well-crystallizable double chlorides with many metallic chlorides. Some of these double salts are almost sure to separate in the test drop as it passes to dryness whenever CsCl is used as a reagent; many are quite characteristic in their habit and in their optical characters. Those which are likely to be met with are tabulated below.

The cesium double chlorides which separate are:

*I. Isotropic; Colorless.*

Octahedra, Cubes.

HgCl <sub>2</sub> ·CsCl	Cubic (also Ortho.)
Cs <sub>2</sub> SnCl <sub>6</sub>	Cubic
PbCl <sub>2</sub> ·2 CsCl	Cubic (?)
AgCl·2 CsCl	Cubic

Hexagonal Plates and Tablets (Basal pinacoids).

SbCl <sub>3</sub> ·2 CsCl·2½ H <sub>2</sub> O	Hex.
2 SbCl <sub>3</sub> ·3 CsCl	Hex.
2 AsCl <sub>3</sub> ·3 CsCl	Hex. (pseudo-cubic)
2 BiCl <sub>3</sub> ·3 CsCl·2½ H <sub>2</sub> O	Hex.
CdCl <sub>2</sub> ·CsCl	Hex.
2 TiCl <sub>3</sub> ·3 CsCl	Hex.

*II. Isotropic; Colored.*

Octahedra.

Yellow —	Cs <sub>2</sub> TeCl <sub>6</sub>
Yellow or Brown —	Cs <sub>2</sub> PdCl <sub>6</sub>
Yellowish Green —	Cs <sub>2</sub> OsCl <sub>6</sub>
Yellow or Orange —	Cs <sub>2</sub> PtCl <sub>6</sub>
Red —	Cs <sub>2</sub> IrCl <sub>6</sub>
Brown —	Cs <sub>2</sub> RuCl <sub>6</sub>

(These cubic salts are Cs salts of complex chloroacids.)

Hexagonal Plates, Tablets (Basal pinacoids).

Yellow —	FeCl <sub>3</sub> ·2 CsCl·H <sub>2</sub> O	Hex.
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*III. Anisotropic; Colorless.*

Pseudo-octahedra —	InCl <sub>3</sub> ·3 CsCl·2 H <sub>2</sub> O	Tetrag.
Rhombic Plates, Tablets —	BiCl <sub>3</sub> ·3CsCl	Ortho.
Rhombohedral Tablets —	CdCl <sub>2</sub> ·CsCl	Hex.
	CdCl <sub>2</sub> ·4 CsCl	Hex.
	PbCl <sub>2</sub> ·4 CsCl	Hex.

Dendrites, Needles, Prisms, Plates.

SbCl <sub>3</sub> ·2 CsCl·2½ H <sub>2</sub> O	Hex.
SbCl <sub>3</sub> ·3 CsCl	Hex.
BiCl <sub>3</sub> ·3 CsCl	Ortho.
CdCl <sub>2</sub> ·CsCl	Hex.
CaCl <sub>2</sub> ·CsCl	Mono. (?)
CeCl <sub>2</sub> ·CsCl	Mono (?)
InCl <sub>3</sub> ·3 CsCl	(?)
PbCl <sub>2</sub> ·4 CsCl	Ortho.

III. *Anisotropic; Colorless (Continued).*

Dendrites, Needles, Prisms, Plates.

$2 \text{ PbCl}_2 \cdot \text{CsCl}$	(?)
$\text{MgCl}_2 \cdot \text{CsCl} \cdot 6 \text{ H}_2\text{O}$	Ortho.
$\text{MgCl}_2 \cdot \text{CsCl}$	(?)
$\text{MnCl}_2 \cdot 2 \text{ CsCl} \cdot 3 \text{ H}_2\text{O}$	(?)
$\text{MnCl}_2 \cdot 2 \text{ CsCl} \cdot 2\frac{1}{2} \text{ H}_2\text{O}$	(?)
$\text{MnCl}_2 \cdot 2 \text{ CsCl} \cdot 2 \text{ H}_2\text{O}$	Triclin. (?)
$\text{MnCl}_2 \cdot 2 \text{ CsCl}$	(?)
$\text{MnCl}_2 \cdot \text{CsCl} \cdot 2 \text{ H}_2\text{O}$	(?)
$\text{HgCl}_2 \cdot \text{CsCl}$	Ortho. and Cubic.
$\text{HgCl}_2 \cdot 3 \text{ CsCl}$	Ortho.
$2 \text{ HgCl}_2 \cdot \text{CsCl}$	Mono.
$5 \text{ HgCl}_2 \cdot \text{CsCl}$	Mono.
$\text{AgCl} \cdot 2 \text{ CsCl}$	Ortho.
$2 \text{ TiCl}_3 \cdot 3 \text{ CsCl}$	Hex.
$\text{TiCl}_3 \cdot 3 \text{ CsCl}$	(?)
$\text{TiCl}_3 \cdot 2 \text{ CsCl}$	(?)
$\text{SnCl}_4 \cdot 2 \text{ CsCl}$	Ortho.
$\text{ZnCl}_2 \cdot 2 \text{ CsCl}$	Mono.
$\text{ZnCl}_2 \cdot 3 \text{ CsCl}$	Tetrag.

IV. *Anisotropic; Colored.*

Dendrites, Needles, Prisms, Plates.

Orange or Red —	$\text{CuCl}_2 \cdot \text{CsCl}$	(?)
	$\text{FeCl}_3 \cdot 2 \text{ CsCl} \cdot \text{H}_2\text{O}$	Hex.
	$2 \text{ FeCl}_3 \cdot 2 \text{ CsCl} \cdot \text{H}_2\text{O}$	(?)
	$2 \text{ FeCl}_3 \cdot 4 \text{ CsCl} \cdot 2 \text{ H}_2\text{O}$	(?)
	$2 \text{ FeCl}_3 \cdot 6 \text{ CsCl} \cdot 2 \text{ H}_2\text{O}$	(?)
	$\text{PdCl}_2 \cdot 2 \text{ CsCl}$	(?)
	$\text{PtCl}_2 \cdot \text{CsCl}$	Tetrag.
	$\text{PtCl}_2 \cdot 2 \text{ CsCl}$	Tetrag.
Yellow —	$\text{UO}_2\text{Cl}_2 \cdot 2 \text{ CsCl}$	Triclin.
Pink —	$\text{MnCl}_2 \cdot 2 \text{ CsCl} \cdot \text{H}_2\text{O}$	Triclin.
Blue —	$\text{CoCl}_2 \cdot \text{CsCl}$	(?)
	$\text{CoCl}_2 \cdot 2 \text{ CsCl}$	(?)
	$\text{CoCl}_2 \cdot 3 \text{ CsCl}$	Tetrag.
Green —	$\text{NiCl}_2 \cdot 3 \text{ CsCl}$	Tetrag (?)

The above list by no means includes all the double cesium chlorides which might separate in the test drop upon an object slide as evaporation takes place. A number of the formulas listed are in doubt. It is probable that some of the compounds should be considered as salts of complex chloroacids rather than "double salts." For more comprehensive discussions of cesium double salts, see: Wagenaar: *Pharm. Weekblad* 50, 273 (1913); Vermande: *Pharm. Weekblad* 55, 1131 (1918); Ducloux: *Mikrochemie* 2, 108 (1924).

Rubidium, potassium, and ammonium also form many "double chlorides" which may separate in concentrated test drops. Some of these salts are isomorphous with the corresponding cesium salts.

NOTE. The addition of cesium chloride may precipitate insoluble or very difficultly soluble normal chlorides, e.g., with  $\text{Ag}^+$ ,  $\text{Hg}^+$ ,  $\text{Pb}^{++}$ ,  $\text{Tl}^+$ , which must not be confused with cesium double chlorides.

## DETECTION OF MERCURY

**Preliminary Tests.**—Since mercury forms two series of salts, mercurous and mercuric, the problem before the analyst is not only the detection of mercury, but he must also decide whether monovalent or divalent mercury is present or a mixture of the two. Mixtures are frequent because of the instability of most mercury salts. A further complication enters into the already difficult problem because mercury is very prone to form “basic” salts of variable composition. Mercurous chloride is insoluble in water, mercurous sulphate and acetate are difficultly soluble, mercurous nitrate is partly hydrolyzed in water but readily soluble in water acidulated with  $\text{HNO}_3$ . Mercuric nitrate is more readily hydrolyzed in water; even in water acidulated with  $\text{HNO}_3$  there is usually obtained on evaporation a basic nitrate.

Test a minute fragment of the unknown material for solubility. (See page 4.) If insoluble, touch a fragment with a tiny drop of dilute  $\text{KOH}$ ; mercurous compounds turn black because of formation of  $\text{Hg}_2\text{O}$ ; mercuric salts turn orange yellow ( $\text{HgO}$ ). If, on the other hand, the substance is water-soluble, test as indicated in Method C.

**A. General Methods Based upon the Reduction to Metallic Mercury and Subsequent Identification.**—Acidify the solution with  $\text{HCl}$ ; introduce into it a tiny piece of pure copper foil or wire 0.5 mm. in diameter and 2 to 3 mm. long. The copper must be bright and clean.<sup>39</sup> Or a similar tiny piece of magnesium may be employed.

The solution is then gently heated for a few minutes over the micro burner or on a water bath or hot plate. The small crucible described on page 17 will be found convenient.

The metallic mercury set free by the action of the copper or magnesium amalgamates with the metal. The copper becomes silvery white and the magnesium silvery or black if sufficient mercury is present to “plate” the metal.

In any event the metal fragment is carefully removed, thoroughly washed and dried, and dropped into a capillary tube closed at one end, made by drawing out a clean piece of glass tubing of high melting point. (See Fig. 29, page 44.) Heat the amalgamated metal in the micro flame until the glass becomes red hot. The mercury will sublime upon the walls of the tube in the form of a grayish ring. Cut the tube at *C* and examine the sublimed mercury under the microscope. Using a bit of glass rod drawn down to the dimension of a hair, rub the film so as to cause the droplets to flow together, examine again, and note that larger

<sup>39</sup> Rubbing with fine emery paper or similar abrasive or dipping in dilute  $\text{HNO}_3$  and washing with distilled water will yield a satisfactory surface.



globules of mercury have been formed. Study the preparation by both transmitted and reflected light so as to be assured that the droplets are opaque, spherical, and exhibit the silvery white luster of metallic mercury. If in doubt, heat the ring of sublimate and thus resublime the mercury.

Confirm the test by converting the mercury into  $\text{HgI}_2$ . This may be readily accomplished by holding the tube horizontal and pushing a tiny fragment of iodine into the capillary tube so that the iodine lies about 5 mm. distant from the globules of mercury. Heat the iodine very carefully so as just barely to vaporize it. Set the tube aside for a short time and heat it again at the point where the iodine lies. Yellow metastable and red stable  $\text{HgI}_2$  are formed, the former usually rapidly changing into the latter. The change from the red to the yellow pseudotetragonal, rhombic form takes place at about  $126^\circ$ .<sup>40</sup> The transformation is enantiotropic and can be readily followed under the microscope. Scratching the yellow dendritic masses when their temperatures have fallen below the transition point causes their immediate transformation into the bright-red stable  $\text{HgI}_2$ . When the heating and cooling have not been too rapid, rectangular plates and prisms, bipyramidal prisms, and irregular dendritic masses are obtained.  $\text{HgI}_2$  melts at  $223^\circ$  to a yellowish-red and finally a red liquid, but the compound sublimes in part before the point of complete fusion is reached. On cooling there is obtained a yellow mass that changes to red. A compound of copper and mercury,  $\text{HgI}_2 \cdot \text{CuI}$ , behaves in a similar manner, but the change from red to yellow takes place below  $100^\circ$ .

A sublimate of metallic mercury can also be obtained when a dry mercurial salt is heated with anhydrous  $\text{Na}_2\text{CO}_3$  or with anhydrous  $\text{CaO}$ . The dry powdered salt of mercury is thoroughly mixed with twice its weight of *freshly ignited*  $\text{Na}_2\text{CO}_3$  or  $\text{CaO}$ ; the mixture is introduced into a tube of the type shown in Fig. 29 and compacted by tapping the tube gently; a little of the reagent is then placed on top of the mixture, the tube above freed from material clinging to the sides, and the mixture heated, the temperature is *slowly* raised until the mixture becomes red hot, and the tube begins to melt. Mercury will be set free and will sublime. Study the sublimate and test as above.

The examination of a sublimate is facilitated if the tube is laid upon an object slide and a large drop of oil of cedar wood (immersion oil) is flowed over the tube at the point where the sublimate has condensed. The annoying refraction image of the glass tube is thus eliminated.

<sup>40</sup> Groth: *Elemente d. physikalischen u. chemischen Krystallographie* (München, 1921), p. 318.

**Experiments.**

(a) Test several mercurous and mercuric salts by heating them with  $\text{Na}_2\text{CO}_3$ . Examine the sublimates. Rub them gently with a hair-like glass rod and note that the globules unite.

(b) Obtain a deposit of Hg upon a tiny bit of Cu foil — 1 mm. by 3 mm. — by heating in a drop of a solution of an Hg salt acidified with HCl. Dry and sublime.

(c) Introduce a fragment of iodine in one or more of the tubes, warm gently, and allow to stand about five minutes. Examine for crystals of  $\text{HgI}_2$ .

**B. Test the Solution with Hydrochloric Acid — HCl.** — To the very dilute solution add the reagent (1 : 4) by Method I.<sup>41</sup>

— Mercurous compounds yield at once a very insoluble, dense, white, somewhat granular precipitate in which no definite crystal form can be discerned even with a high power unless the test drop is exceedingly dilute; then under favorable conditions there may be obtained very tiny slender needles.

Decant and wash the precipitate with warm water. Cause a drop of strong  $\text{NH}_4\text{OH}$  to flow over the white precipitate of  $\text{HgCl}$ ; it turns black owing to the formation of a mixture of Hg and  $\text{HgClNH}_2$ .

This compound, when examined with a high power,<sup>42</sup> will be seen to consist of a mass of tiny acicular crystals, tiny square and rectangular plates, and many fusiform grains.

If the quantity of precipitate is sufficient, decant again and wash, then treat the black compound with a saturated solution of  $(\text{NH}_4)_2\text{SO}_4$ , in which  $\text{HgClNH}_2$  is soluble but metallic mercury is insoluble; the latter can be made to unite into characteristic globules.

Mercuric salts give no precipitate with HCl.

Silver is thrown down as a dense, curdy, white precipitate of  $\text{AgCl}$  which rapidly darkens under the influence of light.  $\text{AgCl}$  is readily soluble in  $\text{NH}_4\text{OH}$  from which it separates, on standing, in isotropic rectangular plates, cubes, and octahedra (Fig. 211, page 355). Similar cubic crystals can be obtained, but less readily, by boiling the curdy  $\text{AgCl}$  with concentrated HCl; treated in this way  $\text{HgCl}$  is also dissolved but separates on cooling in tetragonal plates and prisms, *but no cubes*, and part of the  $\text{HgCl}$  is oxidized to  $\text{HgCl}_2$ .

Lead forms difficultly soluble  $\text{PbCl}_2$ , separating in colorless, or white,

<sup>41</sup> For an extensive discussion of the HCl group in qualitative analysis, see Schoorl: *Zeit. anal. Chem.* 47, 222 (1908).

<sup>42</sup> Cover the preparation with a cover-glass. Great care must be exercised to prevent the objective from coming into contact with the strongly ammoniacal solution, since both copper and nickel are soluble in this reagent. Even  $\text{NH}_3$  vapors will attack the objective mount. After using  $\text{NH}_4\text{OH}$  it is wise to wipe off the objective with lens paper moistened with water and then wipe thoroughly dry.

long, acicular, irregularly ragged prisms, feathery dendritic masses, and X's with characteristic slightly curving arms (Fig. 124, page 183).  $\text{PbCl}_2$  is more soluble in water acidulated with  $\text{HNO}_3$  than in pure water, hence its separation is far from complete; it is readily soluble in hot water from which, on cooling, it separates in thin, well-formed orthorhombic prisms, pseudohexagonal tabular rhombs, and rhombic or six-sided plates (Fig. 125, page 183). Precipitated cold or recrystallized from hot water, the character of the crystal forms obtained will vary with concentration, temperature, and the nature of other metallic ions that may be present. If recrystallized by heating in the presence of salts of the alkalis, double salts are formed which separate on cooling with a very different habit from that of  $\text{PbCl}_2$ ; it is therefore better to decant the mother liquor from the  $\text{PbCl}_2$  which has been precipitated cold, and recrystallize the crystalline residue, rather than heat the test drop as it stands. If in doubt as to the nature of the recrystallized salt, add a fragment of KI; characteristic iridescent yellow plates of  $\text{PbI}_2$  will be formed if lead is present (Fig. 138, page 205).

With thallium ( $\text{Tl}^+$ ),  $\text{TlCl}$  is obtained, separating in white irregular crosses, or clusters of radiating crystals somewhat star-like in appearance (Fig. 121, page 183); cubes and hexagons are also obtained. Since these crystals are generally aggregates that scatter light they appear black by transmitted light.  $\text{TlCl}$  is soluble in hot water, from which it separates on cooling in transparent (or black in appearance) isotropic cubes. KI precipitates  $\text{TlI}$  in forms isomorphous with  $\text{TlCl}$ . The precipitate in the cold is generally sufficiently characteristic for the differentiation of  $\text{Tl}^+$  from  $\text{Pb}^{++}$ , but recrystallization from hot water (after decantation) plus the addition of KI should remove all cause for doubt.

A source of possible error in concentrated solutions may be caused by the separation of complex chlorides of antimony and bismuth; but, if the material has been dissolved in  $\text{HNO}_3$ , concentrated to crystallization, and a drop of water added, the immediate precipitation of antimonyl or bismuthyl salts should be sufficient warning to the analyst to be on his guard.

Tungstates and molybdates in certain concentrations are decomposed by  $\text{HCl}$  (and other mineral acids), tungstic acid and molybdic acid being precipitated. (See page 394.)

In all testing with  $\text{HCl}$  as precipitating reagent the dilute acid should be used, for an excess of concentrated  $\text{HCl}$ , especially if added to concentrated solutions of salts, will cause the separation of many of them because of the forcing back of their dissociation.

**Experiments.**

- (a) Precipitate  $\text{HgCl}$ ; examine with the microscope.
- (b) Add  $\text{NH}_4\text{OH}$  to the white precipitate and examine again.
- (c) Precipitate  $\text{AgCl}$ , and  $\text{PbCl}_2$ , and compare their appearances with that of  $\text{HgCl}$ .

**C. Test the Solution with Potassium Iodide —  $\text{KI}$ . — (Or with  $\text{NaI}$ .)**

*Compounds Formed* —  $\text{HgI}$   
 $\text{HgI}_2$ .

To the moderately concentrated solution add the reagent by Method I, page 31, but in this case the concentration of the reagent should be low, at least at the beginning of the reaction.

Mercurous salts yield a greenish, formless mass of  $\text{HgI}$ , which is soluble in an excess of  $\text{KI}$  with the formation of  $2\text{KI} \cdot \text{HgI}_2$ , and some metallic mercury is usually set free.

Mercuric salts yield brilliant vermilion-red  $\text{HgI}_2$  in tiny rhombs, rectangular plates, and tablets, rosette-like dendritic aggregates, or botryoidal masses. These crystals belong to the tetragonal system (Fig. 111, page 151).

When the flow of the reagent into the test drop is sufficiently slow, pale yellow rhombic plates of metastable  $\text{HgI}_2$  are first formed; they may change almost at once into the stable red iodide, either by solid polymorphic transformation, or by solution and reprecipitation. If the concentration of the reagent is too high,  $\text{HgI}_2$  is immediately dissolved and a colorless solution of  $2\text{KI} \cdot \text{HgI}_2$  results.  $\text{HgI}_2$  is also soluble in an excess of mercuric salts; hence a low concentration of reagent and a high concentration of  $\text{Hg}^{++}$  in the test drop may prevent a satisfactory crystallization of  $\text{HgI}_2$ . It may thus happen that, unless the preparation is closely watched and carefully performed, no evidence of the presence of  $\text{Hg}^{++}$  may be obtained even if much mercury is present; moreover, many other alkali salts and most ammonium salts dissolve  $\text{HgI}_2$  because of its property of uniting with them to form double salts.

To guard against the possibility of error it is usually wise to add to the preparation (after the  $\text{KI}$  has flowed in) a tiny fragment of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The copper will unite with the  $\text{I}^-$  of the  $\text{KI}$ , thus breaking down the double mercury salt and causing the precipitation of red  $\text{HgI}_2$  in its characteristic form.

Lead forms  $\text{PbI}_2$ , bright yellow flakes, and characteristic hexagonal plates (Fig. 138, page 205). These plates when floating and at the proper angle appear greenish or brownish by transmitted light, some-

times even gray. By reflected light they exhibit the brilliant colors of thin films, an extremely characteristic feature of this compound.

Silver is precipitated as  $\text{AgI}$  in a faintly yellow formless mass; but, if the  $\text{KI}$  has been added in excess, a crystalline compound may separate.

Thallium ( $\text{Tl}^+$ ) usually gives merely a fine granular precipitate appearing black by transmitted light, but if conditions are just right crystals similar in appearance to those of  $\text{TlCl}$  are obtained. (See Fig. 121, page 183.)

Cuprous salts give cuprous iodide, a dense white granular precipitate. Cupric salts under certain conditions may also give cuprous iodide and set free iodine, the latter appearing as opaque, black, more or less granular, and rhomb-shaped crystals. In dark-green solutions the white iodide may appear to be greenish, resembling  $\text{HgI}$ .

Salts of antimony in the presence of  $\text{HNO}_3$  may yield with  $\text{KI}$  orange-red crystals, some of which closely resemble those of  $\text{HgI}_2$ , but most of the crystals are hexagonal plates or six-pointed rosettes — the skeletons of the hexagonal plates. This iodide is soluble in  $\text{KI}$  solutions, giving a double iodide whose solubility is sufficiently low to cause it to separate in the test drop in the form of large yellow plates and prisms, singly or more often in bristling aggregates and sheaves or star-like masses. In testing with  $\text{KI}$  solutions containing antimony, iodine is generally set free and a test for mercury may be unobtainable.

Bismuth salts in solution react somewhat like antimony, but, since the tendency to form basic salts (bismuthyl salts) is greater than in the case of antimony, more acid (usually  $\text{HNO}_3$  or  $\text{HCl}$ ) is required to keep a clear solution and consequently iodine is more readily set free and in greater quantity; it follows that bismuth iodide and crystalline double iodides are less readily obtained. Most compounds of arsenic behave like bismuth.

Cadmium, antimony, bismuth, arsenic, and lead interfere with or mask the iodide test for mercury.

Certain compounds of selenium and tellurium give an orange-red or brownish-red crystalline precipitate with  $\text{KI}$ . (See page 160.)

The behavior of potassium iodide with some of the commoner elements can be summarized as follows:

*Character of precipitate:*

Brilliant red crystals.

Orange-red crystals.

Yellow hexagonal iridescent plates.

Yellow needles, plates, and prisms.

*Elements which may be present:*

$\text{Hg}$ . (Red  $\text{HgI}_2$  becomes yellow on heating, enantiotropic.)

( $\text{Hg}$ );  $\text{Cd}$ ;  $\text{Sb}$ ;  $\text{Bi}$ ;  $\text{As}$ ;  $\text{Se}$ ;  $\text{Te}$ ;  $\text{Sn}^{++++}$ .

$\text{Pb}$ .

$\text{Pb}$ ;  $\text{Sb}$ ; ( $\text{Bi}$ ?).

Yellow rhombs.	HgI <sub>2</sub> , metastable.
Greenish granular mass.	Hg; Cu <sup>+</sup> ; Cu <sup>++</sup> .
White or very faintly yellow curdy mass or granular precipitate.	Ag; Cu <sup>+</sup> ; Cu <sup>++</sup> ; Cd(?); Tl <sup>+</sup> .
Brownish-red pulverulent precipitate or tiny, dark red (almost black) disks, with iodine set free.	Hg; Sb; Bi; As; Se; Te; Tl <sup>+</sup> .
Opaque black plates, needles, and dendritic fragments. Solution yellow.	Iodine, set free from KI; Pd.

In testing percussion powders for mercury (fulminate) and antimony (sulphide) it should be borne in mind that powerful oxidizing agents (KClO<sub>3</sub>) may interfere with the ordinary tests.

In such mixtures KI may fail to yield satisfactory tests because of the iodine set free. If the preparations are set aside and allowed to pass to dryness through spontaneous evaporation, HgI<sub>2</sub> will usually separate in identifiable crystals. A far better plan, however, is to spread the powder upon a large object slide and pick out the different components under a hand lens or a Greenough type binocular microscope and then test the separated components individually.

#### Experiments.

- (a) Precipitate HgI<sub>2</sub> with KI. Note the effect of adding an excess of the reagent. Then add CuSO<sub>4</sub> to remove the excess iodide.
- (b) Add KI to a solution of HgNO<sub>3</sub>.

#### D. To the Solution Add Potassium Thiocyanate and Zinc Sulphate.

*Compound Formed* —  $\text{Zn}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2$ .

Mercurous salts give no characteristic reaction; but mercuric salts yield  $\text{Zn}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2$  (Fig. 96, page 139). This compound has already been discussed under zinc. (See page 137.)

The addition of a little copper or cobalt acetate greatly increases the sensitivity of the reaction.

To perform the test, proceed as follows. To the moderately concentrated neutral test drop add a small fragment of KSCN; stir thoroughly. If a precipitate is formed, add more reagent. Place adjacent to this drop, a drop of water in which is dissolved a very little  $\text{ZnSO}_4 \cdot 5\text{H}_2\text{O}$  and a *trace* of a copper or cobalt salt. Cause the test drop to flow into the zinc solution. If mercury is present, characteristic crystals of  $\text{Zn}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2$  will appear. These crystals will be colored by the copper or the cobalt as has already been described. (See Zinc, page 140.)

When dealing with relatively pure salts of mercury this test leaves little to be desired, but in complex mixtures, it is difficult properly to

adjust the concentration of the KSCN; this is especially true if a precipitate is obtained which does not dissolve in an excess of the reagent. When the test drop is turbid, it is best to decant, centrifuge, or filter before the drop is caused to flow into the drop containing the zinc or cobalt.

#### Experiments.

See under Zinc, Method A, page 136.

#### E. Test the Solution with Potassium Bichromate — $K_2Cr_2O_7$ .

This reaction should be regarded as a confirmatory test for the presence of mercurous compounds rather than one useful for the identification of mercury. Its sensitivity is very low and there are many interfering elements and conditions. The reaction, however, is a most interesting one, particularly from the viewpoint of crystallization phenomena.

The test drop should be concentrated with respect to  $Hg^+$  and should be strongly acidified with  $HNO_3$  (1 : 4). The reagent may be added by Method I or by Method II to the test drop at room temperature, or heated to the boiling point; in the latter case there is danger of oxidizing  $Hg^+$  to  $Hg^{++}$ .

Mercuric compounds yield no crystalline precipitate.

Mercurous salts are precipitated as mercurous chromate  $Hg_2CrO_4$ . There is first formed a dark-red (black by transmitted light), fine, granular precipitate which immediately develops into spherical grains, disks, and globular masses; these in turn become drusy and grow into irregular aggregates of radiating, short, stout prisms with rounded or angular ends or crosses and dendrites are formed (Fig. 110, page 151). In a few minutes aggregates closely resembling lichens are formed. These lichen-like aggregates and the skeleton crosses are very characteristic.

If the reaction has been performed by Method II in a hot solution, thin, square plates and crosses predominate. These plates show the colors of thin films and appear lemon-yellow by transmitted light. If the preparation contains an excess of the mercurous salt and is boiled, there may be formed a basic salt<sup>43</sup>  $Hg_2O \cdot 2 Hg_2CrO_4$  crystallizing in dark-red needles.

Lead precipitated in hot  $HNO_3$  solutions gives crystalline aggregates closely resembling those of  $Hg_2CrO_4$ , but most of the crystals are rhombs and tiny, well-formed prisms. These crystals are soluble in NaOH (distinction from  $Hg_2CrO_4$ ).

<sup>43</sup> Fichter and Oesterheld: *Zeit. anorg. Chem.* 76, 347 (1912).

Silver yields large, dark-red pleochroic plates and scales which may often mask the test for  $\text{Hg}^+$ . (See Silver, page 280; Fig. 210, page 355.)

Strontium, barium, cadmium, zinc, and manganese yield insoluble or difficultly soluble chromates and therefore interfere.

#### Experiments.

Test with  $\text{K}_2\text{Cr}_2\text{O}_7$  as above both mercurous and mercuric salts, with and without  $\text{HNO}_3$  present, in both cold and hot solutions.

#### F. Other Tests for Mercury.

(a) *Diphenylcarbazide* forms with salts of  $\text{Hg}^{++}$  blue-violet amorphous " precipitates and very dark-colored spherulites. With  $\text{Hg}^+$  an identically colored precipitate is obtained *but no spherulites*.

Prepare the reagent as described under Magnesium Method C, page 133, and adjust its concentration.

For reactions with other cations, see pages 134, 135.

(b) The blue color of iodized starch is destroyed by salts of mercury and salts of silver. According to Korenman, this reaction is specific for these two elements.<sup>44</sup>

Originally proposed as a test-tube reaction, it may be conveniently modified for microscopical analyses as follows. To a small drop of water upon an object slide add a little potato or canna starch, stir well, and examine under the microscope to make certain of even dispersion and absence of lumps. Add a very small drop of a light yellow solution of iodine in potassium iodide, stir well, and again examine the preparation. The starch granules should all be blue, not black, and there must be no uncolored granules. To the reagent thus obtained add at the center of the drop a minute dry fragment of the material to be tested (preferably in the form of nitrate). As the fragment dissolves in an outward enlarging circular zone, the blue color of the starch granules within the zone will be discharged if mercury (or silver) is present. The progressive movement of the salt solution can be easily followed because of an advancing zone of granulate precipitate. If the dry fragment is very small, the advancing zone of solution moves sufficiently slow to permit observations of the decoloration of the blue granules just as they are engulfed. The change is from blue to colorless without immediate alteration in the morphological appearance of the granules. The preparation should be studied immediately after the introduction of the fragment of the material to be tested. Many salts cause a swelling of the granules and a brown color with eventual disintegration.

<sup>44</sup> *Mikrochemie* 14, 182 (1933).



In confirmation of Korenman's statements we have found no cations which cause the immediate change from blue to colorless. The test is not interfered with by the presence of other heavy metals. Alkalis and strong acids must be absent.

### DETECTION OF BERYLLIUM

#### A. By Means of Chloroplatinic Acid — $\text{H}_2\text{PtCl}_6$ .

*Compound Formed* —  $\text{BePtCl}_6 \cdot 8\text{H}_2\text{O}$ .

The test is performed by Method III, page 35. In order that the results may be satisfactory, it is essential that the dry film shall contain a high concentration of beryllium and that members of the group of the alkalis shall be absent or present in little more than traces.

$\text{BePtCl}_6 \cdot 8\text{H}_2\text{O}$  separates in hygroscopic, faintly yellow, square and rectangular plates and rectangular prisms of the tetragonal system (Fig. 53, page 77). The crystals usually occur singly, but penetration twins are also formed; their solubility is somewhat less than that of  $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and their separation from solution can be induced by the addition of alcohol. This is most easily accomplished by applying a large drop of alcohol to the object slide near the test drop and immediately tipping the slide so as to cause the drop of alcohol to flood the preparation. Holding the slide well inclined prevents the alcohol from spreading over the whole surface, and in a few seconds it may be placed on the microscope stage for examination.

If the addition of the reagent causes an immediate precipitation of the potassium group, an excess of the reagent should be added, the solution decanted from the precipitated chloroplatinates, and more chloroplatinic acid added to the decanted liquid in order to ensure a sufficient excess. Evaporation must be resorted to and even then  $\text{BePtCl}_6 \cdot 8\text{H}_2\text{O}$  will seldom crystallize well unless the air of the laboratory is very dry. Usually it is necessary to use alcohol in which the beryllium salt is much less soluble.

The crystalline residue obtained should always be examined with crossed nicols. Beryllium chloroplatinate exhibits parallel extinction and is only weakly birefringent; the corresponding sodium salt is strongly birefringent, shows brilliant polarization colors and oblique extinction (triclinic). The potassium group gives isotropic salts. (See Potassium, page 65.)

In our experience this test for beryllium is valueless unless the material tested is so high in beryllium as to constitute a fairly pure salt of this element.

**B. By Means of Potassium Oxalate —  $K_2C_2O_4$ .**

*Compound Formed* —  $K_2C_2O_4 \cdot BeC_2O_4$ .

To the concentrated neutral test drop add a little acetic acid; then add the potassium oxalate by Method II, page 33, but in this case the fragment of reagent must be more than twice as large as is usual in microscopical analysis.

$K_2C_2O_4 \cdot BeC_2O_4$  separates in large, stout, clear, colorless, monoclinic prisms; singly, in twins, or in groups of radiating, irregularly formed prisms. Thin plates in the form of rhombs are also obtained. The salt is strongly birefringent and exhibits an extinction angle of about  $39^\circ$  (Fig. 83, page 111).

Unless the reagent is present in sufficient excess, the test is apt to prove unsatisfactory. Acid potassium oxalate or the oxalates of sodium or ammonium are not suitable reagents.

During the disintegration and solution of the reagent fragment, well-formed crystals of  $K_2C_2O_4$  usually appear *momentarily*. These crystals often bear a striking resemblance to the double salt, and it is therefore imperative that the analyst shall be on his guard lest he fall into error through too hasty a decision.

Certain salts (*e.g.*,  $HgCl_2$ ), if present in the drop being tested, have the property of inducing potassium beryllium oxalate to crystallize in long prisms. Behrens<sup>45</sup> has therefore suggested that a little  $HgCl_2$  be added to the test drop before the fragment of reagent is introduced in order to ensure the formation of elongated prisms, thus differentiating the double salt from crystals of  $K_2C_2O_4$ .

Many other elements form normal or double oxalates. (See Calcium, page 120.)

$K_2C_2O_4 \cdot BeC_2O_4$  can be readily recrystallized by gently warming the preparation until the salt passes into solution; on cooling, large well-formed characteristic crystals are obtained. These crystals are soluble in a solution of ammonium carbonate, a property which can be made use of when there is doubt as to the nature of the compound obtained.

Note well that this microscopical oxalate test for Be appears to be at variance with the statement commonly made that Be yields no precipitate with oxalic acid or alkali oxalates and that this failure to react serves to differentiate Be from Zr and the rare earths.

It is obvious that this statement applies to dilute test-tube reactions only.

**C. By Means of Diphenylcarbazide.**

Prepare and adjust the concentration of the reagent and perform the test as suggested under Magnesium, Method C, page 133.

<sup>45</sup> *Anleitung*, p. 45. Behrens-Kley: *op. cit.*, p. 48.

Beryllium yields immediately an "amorphous" precipitate, followed by the formation of symmetrical radiates of fine needles or thin elongated scales mostly on edge. These spherulites are brown by transmitted light and are almost opaque. They exhibit moderate double refraction and the characteristic black cross of radiates of anisotropic acicular crystals.

Aluminum yields spherulites indistinguishable from those formed by beryllium. (See page 133.)

None of the common cations appear to interfere with this test save when they are present in excess and the  $\text{Be}^{++}$  (or  $\text{Al}^{+++}$ ) is present in very low percentage only; under these conditions the test may be masked by dense, dark-colored precipitates.

#### TREATMENT OF MIXTURES—SECONDARY GROUP OF GROUP II

(a) *Test for  $\text{PO}_4$* —by molybdate method, page 339. If phosphates are present, remove the  $\text{PO}_4$ —by treatment with tin in  $\text{HNO}_3$  solution, proceeding as follows. Add strong  $\text{HNO}_3$ , then a few pieces of *pure tin* foil or granulated tin. Boil until all the metallic tin has been converted into insoluble metastannic acid. Decant, or filter, and repeat the treatment until no test for  $\text{PO}_4$ — is obtained. Evaporate the solution to dryness and test a portion for arsenic. If arsenic is found, ignite the residue until all arsenic is driven off. Extract the residue with water acidified with  $\text{HNO}_3$  and test as below.

In order that the removal of all the  $\text{PO}_4$ — may be successfully accomplished, it is essential that the concentration of the  $\text{HNO}_3$  in the test drop shall be sufficiently high and that no excess of metallic tin shall have remained undissolved.

The treatment is best performed in the small glass crucible shown in Fig. 10, page 17, or in a tiny test-tube rather than attempted upon an object slide or in a small watch-glass.

(b) *Remove the alkaline earths, lead, and silver*, by precipitation with  $\text{H}_2\text{SO}_4$ ; filter; evaporate the filtrate and fume off the excess of  $\text{H}_2\text{SO}_4$ .

(c) *Separation of Beryllium*.—Treat the weakly acidified drop with iron foil to remove metals more electronegative than iron. (See page 401.)

Add  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{O}_2$ ; warm gently for a time, evaporate, and repeat the treatment. Extract the residue with a concentrated solution of  $(\text{NH}_4)_2\text{CO}_3$ .  $\text{Be}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{U}^{++++}$ ,  $\text{Mg}^{++}$  may be present in the solution. Evaporate, dissolve in dilute  $\text{HCl}$ , add a little acetic acid, and test with  $\text{K}_2\text{C}_2\text{O}_4$ .

If much  $\text{Mg}^{++}$  is present, add to the acid solution  $\text{NaOH}$  in which  $\text{Mg}^{++}$  is insoluble; the solution may contain  $\text{Be}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Al}^{+++}$ .

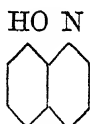
(d) *Separation of Magnesium from Beryllium, Zinc, Cadmium, and Aluminum.*—Precipitate with NaOH, warm, evaporate, extract the residue repeatedly with small amounts of water.  $\text{Mg}^{++}$  and some  $\text{Cd}^{++}$  remain undissolved. Dissolve the insoluble portion in HCl and divide into two portions; test one portion for  $\text{Mg}^{++}$  with  $\text{HNa}_2\text{PO}_4$  and the other for  $\text{Cd}^{++}$  by the thiocyanate method.

(e) *Separation of Zinc from Beryllium, Magnesium, and Cadmium.*—Ignite the material *gently*, and warm with a strong solution of NaOH.  $\text{Zn}^{++}$  and  $\text{Be}^{++}$  are dissolved. Decant, acidify with acetic acid, and precipitate the  $\text{Be}^{++}$  as oxalate. (Some  $\text{Zn}^{++}$  is always precipitated with the  $\text{Be}^{++}$ .) Decant, evaporate the clear solution to dryness, and destroy the oxalate ion by  $\text{H}_2\text{SO}_4$  and heat. Take up the residue with water (acidify if necessary), add  $(\text{NH}_4)\text{C}_2\text{H}_3\text{O}_2$  and test for  $\text{Zn}^{++}$  by the thiocyanate method (page 136).

(f) *Separation of Beryllium from the "Rare Earths."*—To a moderately dilute solution add oxalic acid and boil.  $\text{Be}^{++}$  remains in solution, the rare earths and  $\text{Zn}^{++}$  are precipitated. Or precipitate the moderately concentrated solution with a saturated solution of  $\text{K}_2\text{SO}_4$ . Be remains in solution; the rare earths of the potassium sulphate group are insoluble.

(g) *Separation of Beryllium from Aluminum.*—Add  $(\text{NH}_4)_2\text{CO}_3$  in excess. Both  $\text{Al}^{+++}$  and  $\text{Be}^{++}$  are at first precipitated, but the  $\text{Be}(\text{OH})_2$  is soluble in excess of  $(\text{NH}_4)_2\text{CO}_3$ . Repeat the precipitation and re-solution several times.

(h) Fuse the material with an excess of  $\text{Na}_2\text{CO}_3$ . Extract with water. Be will be found in the insoluble residue as oxide; the Al passes into solution as an aluminate.

Separations by Means of 8-Hydroxyquinoline. —  The H

in the OH group has acidic properties and can be replaced by a metal. Few of these "quinolates" separate in well-formed crystals.

#### A. In Acetic Acid-Ammonium Acetate Solution.<sup>46</sup>

*Not Precipitated.*

Li, Na, K, Rb, Cs;

Be, Mg, Ca, Sr, Ba;

Ge, As, Se, Te, Pb, Pt;

V, Cr, Mn, Ru, Rh, Os, Ir, Au, Tl, Sn, Sb.

<sup>46</sup> Lundell and Hoffman: *Outlines of Methods of Chemical Analysis* (Wiley, New York, 1938), p. 115.

Fresenius, Fresenius, and Frommes: *Zeit. anal. Chem.* 96, 433 (1934).

**B. In Ammoniacal Solution.**<sup>46</sup>*Not Precipitated.*

Li, Na, K, Rb, Cs;

Ca, Sr, Ba;

Ge, As, Se, Te, Pt;

V, Cr, Mo, W, Ru, Rh, Os, Ir, Ag, Au, Co, Ni, Sn, Sb, Tl, Pb.

In the tabulation above the second group of elements, Ge, etc., are partly precipitated when present in large amount. 8-Hydroxyquinoline in buffered acetic acid solution is one of the most satisfactory reagents for the separation Be from Al.

## CHAPTER V

### THE DETECTION OF THE ELEMENTS OF GROUP III

B; Sc, Y, La, Yb; Al, Ga, In, Tl

Group III of the Periodic Classification of the elements comprises (1) the transitional element boron, (2) a group of the rare earths, scandium, yttrium, lanthanum, and ytterbium, (3) the aluminum group comprising aluminum, gallium, indium, and thallium.

Boron is essentially an acid-forming element, and it is rare indeed that the analyst is called upon to detect boron in material other than borates. Boron forms acids having the formulas,  $\text{HBO}_2$  — metaboric acid;  $\text{H}_3\text{BO}_3$  — orthoboric acid;  $\text{H}_2\text{B}_4\text{O}_7$  — tetraboric acid. Most of the salts of metaboric acid can be crystallized but they are unstable and are readily decomposed by carbon dioxide yielding tetraborates. Although orthoboric acid exists free in a stable crystalline state as the "boric acid" of commerce, none of its salts are known. The borates which the analyst is likely to encounter in his work are partly decomposed metaborates and, ordinarily, tetraborates.

The element boron resembles carbon and silicon, but in its salts the resemblance approaches beryllium, aluminum, and scandium; in spite of these resemblances, however, we have no boron compounds related to these elements suitable for microchemical identity reactions.

The only compounds of sufficiently characteristic habit are derivatives of the acid  $\text{HBF}_4$ ; but unfortunately, the alkali salts of this acid are isomorphous with the corresponding fluosilicates, fluotitanates, fluozirconates, and fluogermanates, and hence can be of but limited value in the analysis of complex mixtures.

The elements falling in the subgroup consisting of scandium and the "rare earths" have practically no analytical analogies with the reactions employed for the identification of members of the other subgroup of Group III, but react more like the alkaline earths. Since it is not practicable to discuss the chemical properties of the scandium group without considering also that group of the rare earths not readily classified in the Mendeléef Periodic Table, we have thought it wise to defer all consideration of the rare earths until after the elements of Group VIII have been discussed. On pages 308–313 will be found a

presentation of the properties upon which the microscopical detection of the rare earths can be based.

The elements in the aluminum group, consisting of aluminum, gallium, and indium, are all closely related; they (especially indium and gallium) also behave in some respects like beryllium, zinc, and cadmium, but their identification tests bear little resemblance to the elements of Group II. In their stable salts they are trivalent, and because Group III approaches the center of the Periodic Table acidic properties begin to make their appearance. Most of their salts hydrolyze if boiled in neutral aqueous solution. The hydroxides of aluminum, gallium, and indium are readily soluble in strong solutions of NaOH and KOH,<sup>1</sup> forming compounds of the type  $M(\text{ONa})_3$  or  $M(\text{OK})_3$ . These compounds exhibit a marked difference in stability. The aluminates and gallates are quite stable, but  $\text{In}(\text{OH})_3$ , though apparently passing into solution in NaOH or KOH, separates on standing and is immediately precipitated on warming. Gallium hydroxide differs from  $\text{Al}(\text{OH})_3$  and  $\text{In}(\text{OH})_3$  in being readily soluble in  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$  and is even soluble (but with difficulty) in  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  solutions.

When the members of the aluminum group occur singly, their property of forming easily crystallizable double sulphates — “alums” — affords one of the most satisfactory reactions for their recognition. But obtaining the characteristic crystals of an alum is merely indicative of the presence of one or more of a group of elements. The general formula of these isotropic double sulphates is  $N_2\text{RO}_4 \cdot M_2(\text{RO}_4)_3 \cdot 24\text{H}_2\text{O}$  — or simplified,  $NM(\text{RO}_4)_2 \cdot 12\text{H}_2\text{O}$ , in which  $N$  may be  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Ag}^+$ ,  $\text{Tl}^+$ , or  $\text{NH}_4^+$ ;  $M$ ,  $\text{Al}^{+++}$ ,  $\text{Ga}^{+++}$ ,  $\text{In}^{+++}$ ,  $(\text{Tl}^{+++})$ ,  $\text{Cr}^{+++}$ ,  $\text{Mn}^{+++}$ ,  $\text{Fe}^{+++}$ ; and  $R$ ,  $\text{S}$ , or  $\text{Se}$ . All these double sulphates are isotropic and form an isomorphous series.

The members of the aluminum group form with the salts of the alkalis a large number of double salts other than the “alums.” With the exception of the “alums” these double salts are nearly all anisotropic; many of them crystallize readily and have a sufficiently characteristic habit to render them of analytical value.

With HF and the alkali metals double fluorides are formed, some of which can be utilized to good advantage, especially in the analysis of silicates and silicious materials where simpler and more convenient methods are not practicable.

The element thallium, like the other elements of high atomic weight, gold in Group I, mercury in Group II, and lead in Group IV, differs markedly in chemical properties from the characteristic properties of

<sup>1</sup> Providing chromium is absent; see Chromium, page 243.

the group in which it falls. Thallium forms two series of salts, thallous ( $Tl^+$ ) and thallic ( $Tl^{+++}$ ); the latter are unstable in aqueous solution and change into thallous compounds if their solutions are boiled. In analytical practice we are concerned with solutions containing thallous compounds only.

Thallium resembles the elements of the potassium group in the formation of an isotropic, difficultly soluble chloroplatinate,  $Tl_2PtCl_6$ ; it resembles  $Ag^+$ ,  $Hg^+$ , and  $Pb^{++}$  in forming a chloride, bromide, and iodide of low solubility; it resembles the alkaline earths, silver (and lead), in that it forms a sulphate of somewhat low solubility. Unlike the members of the aluminum group, thallium does not form "alums." Thallium is the strongest base in Group III, the basicity in the vertical groups increasing with the atomic weight.

### DETECTION OF BORON

#### A. By Means of Turmeric (Curcumin).

*Compound Formed* — "Rosocyanine."

The reagent is applied by Method VI, page 38.<sup>2</sup>

Place a drop of the solution to be tested upon an object slide. Acidulate with dilute  $HCl$ , to decompose any borates present and set free boric acid. Introduce into the drop thus prepared a piece of the reagent-carrying fiber about 5 mm. long, being sure to immerse it completely in the liquid. Allow the drop to evaporate spontaneously to complete dryness, or hasten the evaporation by *very gentle* warming. Cool and examine the fiber under the microscope. A rose or violet-rose color is indicative of the presence of boron. To confirm the reaction, place upon the dry fiber a drop of a 1 per cent solution of  $NaOH$ ; the rose color should immediately change to a clear Prussian blue which in turn gradually becomes violet and pleochroic.<sup>3</sup> There appear to be no interferences other than those given below.

Too high a temperature during evaporation or failure to allow the test drop to go completely to dryness may lead to negative results.

Too high a concentration of the alkali will interfere with the formation of the blue color, and, since the clear blue color is quite fugitive if only traces of boron are present, it is essential that the fiber be examined *immediately* after the application of the  $NaOH$ .

Mineral acids, other than boric acid, give a yellow or brown color to

<sup>2</sup> The preparation of viscose-rayon fibers impregnated with curcumin is described on p. 423.

<sup>3</sup> Chamot and Cole: *Ind. Eng. Chem.* 10, 48 (1918).

Steidler: *Mikrochemie*, 2, 131 (1924).



the fiber on evaporation; furthermore, the addition of the alkali produces a deep brown, never a blue color.

Hygroscopic salts should be absent since they prevent complete drying of the fiber, but if much boron is present the test may succeed in the presence of considerable retained moisture.

Powerful oxidizing (bleaching) substances must be absent, or their characteristic properties must be destroyed before adding the reagent fiber.

Much free phosphoric or silicic acid interferes with the test, rendering the detection of boron exceptionally difficult.

A pink or red color is also given to turmeric by compounds of molybdenum, titanium, zirconium, columbium, tantalum, and metasilicates, but in none of these pink or red reactions does the addition of alkali change the color to any shade or hue of blue.

Since this test for boron is extraordinarily delicate ( $0.025 \mu\text{g.}$ ), object slides containing no boron must be used. It is also obvious that glassware containing boron must never be used in preparing or handling material that is subsequently to be tested for the presence of boron. It is therefore wise always to perform a "blank" test in order to be assured of the purity of the reagents and apparatus employed.

Boric acid can be distinguished from a borate or detected in the presence of a borate as follows: Introduce a turmeric dyed fiber into the test drop and evaporate to dryness without the addition of hydrochloric acid. A rose-pink color turned blue by alkali indicates the presence of free boric acid. Borates yield no rose color. However, it must be remembered that in the presence of inorganic compounds which have the property of decomposing borates a positive test may be obtained without the addition of a strong acid. A number of organic acids have the power of displacing boric acid from a borate.

Ferric salts, particularly if present as ferric borate, interfere with the curcumin reaction.

The rose-colored compound, which turns blue with alkalis, was given the name "rosocyanine" by Schlumberger;<sup>4</sup> its true structure is still in doubt, but it is known that it contains no boron.

#### B. By Means of Ammonium Bifluoride ( $\text{NH}_4\text{F} \cdot \text{HF}$ ) and Potassium or Cesium Chloride.

*Compounds Formed* —  $\text{KBF}_4$   
 $\text{CsBF}_4$ .

Before employing this method, observe all the special precautions directed on page 43, Method X.

<sup>4</sup> *Bul. soc. chim.* (2) 5, 194 (1866).

To the concentrated solution, add a large fragment of  $\text{NH}_4\text{F} \cdot \text{HF}$ ; stir with a platinum wire until the  $\text{NH}_4\text{F} \cdot \text{HF}$  is dissolved; next add a drop of  $\text{HCl}$  (1 : 2), and finally add a crystal fragment of  $\text{KCl}$  or  $\text{CsCl}$ . The entire operation must be performed upon a celluloid slide. After standing several minutes orthorhombic crystals of the double salt begin to separate in the form of square, rectangular, and rhombic plates, having acute angles of  $77^\circ$ , which grow into tabular crystals with beveled edges; these in turn elongate and become rectangular prisms with square or pyramidal ends. (See Fig. 114, page 173. The preparation from which this photograph was made was allowed to pass to dryness.) Their refractive index is so close to that of the mother liquor (between 1.32 and 1.34) that they are almost invisible and require very careful adjustment of the illumination to disclose their true form. The sodium salt, like that formed with silicon, sometimes exhibits the Christiansen effect. (See Sodium, page 63, and also *Vol. I*, page 190.)

Hydrofluoric acid is employed by some analysts rather than ammonium bifluoride or ammonium fluoride because it introduces less crystallizable material into the test drop and reacts more promptly and vigorously; but it is less convenient, requires more care to prevent the spreading of the test drop on the cellulose slides, and there is far more danger in its manipulation.

In order that the crystals may be more readily found it is best to allow the preparation to stand and evaporate to dryness and thus eliminate the effect of the refractive index of the mother liquor.

Instead of double salts we may properly consider that we have to deal with salts of fluoboric acid  $\text{HBF}_4$ . The ammonium, potassium, rubidium, and cesium salts appear to be isomorphous.

The cesium fluoborate test would be an excellent one were it not that a number of other elements form, with cesium salts and  $\text{HF}$ , compounds of sufficiently low solubility to separate on the object slide. Hence the usefulness of the test is restricted to confirmation only, and is of little value in complex mixtures containing any of the interfering elements discussed below.

Aluminum is precipitated as  $\text{Cs}_3\text{AlF}_6$  in tiny cubes too small to be resolved with safety;<sup>5</sup> but, if  $\text{KCl}$  is substituted for  $\text{CsCl}$ , well-formed octahedra and cubes result, of sufficient size to constitute a satisfactory

<sup>5</sup> Very minute crystals are objectionable as a test where  $\text{HF}$  is present, since they require a high-power objective for their recognition and the free working distance of such objectives brings the front lens so close to the drop as to endanger the front lens of the objective. The preparation should always be covered with thin celluloid or viscose.

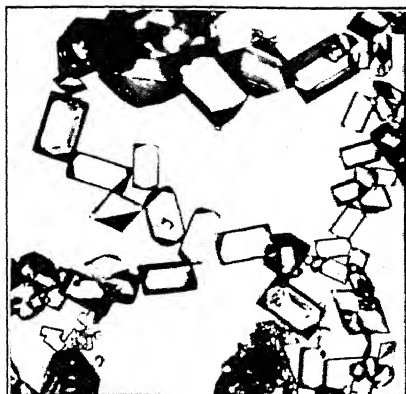


FIG. 114. Boron with Potassium Fluoride. 200X.

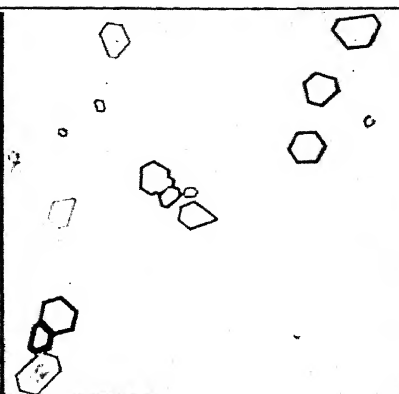


FIG. 115. Germanium with Potassium Fluoride. 200X.



FIG. 116. Titanium with Potassium Fluoride. 100X.

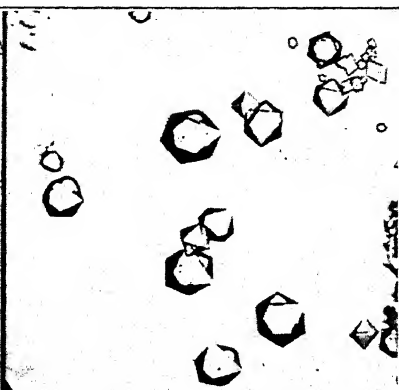


FIG. 117. Zirconium with Ammonium Fluoride and Rubidium Chloride, 100X.



FIG. 118. Indium with Cesium Chloride. 100X.

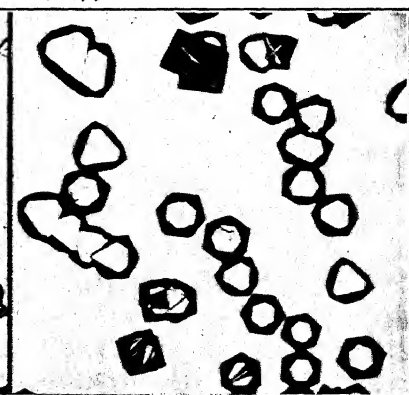


FIG. 119. Indium with Hexamethylenetetramine. 150X.

test for aluminum. The potassium group salts are isomorphous; their solubilities decrease with the rise in atomic weight; all belong to the cubic system, but the sodium salt is monoclinic.  $K_3AlF_6$  is probably a double salt  $3 KF \cdot AlF_3$  but may be regarded as a salt of the hypothetical fluoaluminic acid —  $H_3AlF_6$ .

Indium chloride treated as above rarely gives a fluoindate, but yields instead cesium indium chloride. (See Indium, page 181; Fig. 118, page 173.)

Gallium gives a granular precipitate of a fineness so great, even in dilute solutions, as to appear to be non-crystalline; occasionally a preparation may be obtained in which there can be seen tiny irregular sandy grains more or less rounded, single, or so grouped as to resemble tiny rods.

Titanium, chromium, iron, and vanadium also form, with the potassium group and HF, compounds analogous to those of boron and aluminum; but zirconium, silicon, germanium, and lead form salts derived from the hypothetical acid  $H_2RF_6$ . Considering the compounds as double salts, their composition may be expressed by the formula  $2 MF \cdot RF_3$ , where  $M$  is an alkali metal and  $R$  either Zr, Si, Ge, or Pb. (See Figs. 115, 116, 117, page 173.)

In testing materials of unknown composition, with an alkali salt and HF, we may expect, as the drop goes to dryness, that any of the above double salts may make their appearance. In addition to this troublesome feature there is another, already referred to; namely, that in this group of fluorine compounds, the refractive indices are all so nearly those of the mother liquors as to render difficult the recognition of the salts.

### C. By Means of Concentrated Hydrochloric Acid.

The addition of strong HCl (1 : 1) to an almost saturated solution of a borate precipitates orthoboric acid as flakes, six-leaved rosettes, or three- or six-sided triclinic (pseudo-hexagonal) tablets. Prismatic crystals, showing knee twins (Fig. 95, page 135) or dislocations are often numerous; they correspond to greatly thickened edge views of the platy crystals. Birefringence for the prism view is strong, and for light vibrating parallel to the elongation the visibility in a saturated solution is low ( $n_\alpha = 1.34$ ). Prisms give high-order polarization colors; plates, usually only first order gray or white.

$H_3BO_3$  is only moderately soluble in cold water, but readily so in hot water. At boiling temperatures it passes off in the steam from which it can be condensed in badly formed crystals; these can be recrystallized for identification and subjected to confirmatory tests.

DETECTION OF THE ELEMENTS OF THE ALUMINUM  
GROUP, Al, Ga, In

These three elements are so closely related in their chemical behavior that their microchemical identification is very difficult in material in which two or more are present, especially when one of them is in minute amount only. This is particularly true if the quantity of material available for analysis is also small; for, although separation methods on a test-tube scale are practicable, these same methods applied to drops of solution are rarely dependable.

The usual procedure is based upon differences in the solubilities of the hydroxides, but these hydrous oxides are so easily peptized or changed into negative sols that extraordinary difficulty may be met in dealing with these compounds in drops on an object slide. Moreover, the presence of organic acids will usually prevent the precipitation of the hydroxides.

The group is precipitated with  $\text{NH}_4\text{OH}$  in the presence of  $\text{NH}_4\text{Cl}$ , only sufficient  $\text{NH}_4\text{OH}$  being used to keep copper, nickel, and cobalt in solution, if these elements are present. Gallium may be lost in this treatment. The precipitated hydroxides must be washed with water containing a little  $\text{NH}_4\text{Cl}$  to avoid peptization.

Theoretically the separation should then not be difficult, for warming the hydroxides with  $\text{NaOH}$  or  $\text{KOH}$  should yield soluble aluminates, gallates, and indates, and the indate first formed should hydrolyze on heating and be reprecipitated as  $\text{In}(\text{OH})_3$ . The difficulty arises in the practical impossibility of properly adjusting concentrations when dealing with mere traces of precipitates. The second step is based upon the fact that  $\text{Ga}(\text{OH})_3$  is readily soluble in  $(\text{NH}_4)_2\text{CO}_3$  solution, but  $\text{Al}(\text{OH})_3$  is insoluble in this reagent. Since zincates and cadmates may be formed in the treatment with fixed alkalis, it is always essential to test for the presence of these elements before attempting a separation of the aluminum group.

This hydroxide separation, though practicable, is never sharp and leaves much to be desired.

Gallium can be separated from aluminum and indium by precipitation with  $\text{K}_4\text{Fe}(\text{CN})_6$  in a solution weakly acidulated with  $\text{HCl}$ . Filter or centrifuge, and wash the precipitate with warm  $\text{HCl}$ . Dissolve the precipitate in aqua regia; evaporate to small bulk; add  $\text{HCl}$  and heat until all oxides of nitrogen are expelled. Neutralize with  $\text{NaC}_2\text{H}_3\text{O}_2$ , add acetic acid, and precipitate iron by a solution of alphanitroso-beta-naphthol in 50 per cent acetic acid. Filter or centrifuge. Make the filtrate alkaline with  $\text{NH}_4\text{OH}$  and boil until  $\text{Ga}(\text{OH})_3$  is pre-

precipitated.<sup>6</sup> Wash, dissolve in  $\text{H}_2\text{SO}_4$ , and test with  $\text{Cs}_2\text{SO}_4$  and with  $\text{K}_4\text{Fe}(\text{CN})_6$ .

### A. By Means of Cesium Sulphate — $\text{Cs}_2\text{SO}_4$ .

*Compounds Formed* —  $\text{CsAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$  .  
 $\text{CsGa}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$   
 $\text{CsIn}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ .

To the drop to be tested  $\text{NH}_4\text{OH}$  is added to precipitate the hydroxide, the supernatant liquid is decanted, and the precipitate washed once.<sup>7</sup>

To the precipitate dilute  $\text{H}_2\text{SO}_4$  is added a *very little* at a time until the precipitate is practically completely dissolved, but using care to avoid an excess of acid. If too concentrated a solution is obtained, add a drop of water.

To the test drop thus obtained, add the  $\text{Cs}_2\text{SO}_4$  by Method II, page 33.

Cesium "alum" separates in large, well-formed, brilliant, colorless octahedra, or combinations of the cube and octahedron (Fig. 112, page 151). Elongated octahedra and octahedra flattened parallel to two diagonally opposite faces are also common.

In solutions that are too concentrated or that have evaporated too rapidly, dendritic forms and many-faced crystal aggregates are obtained. In such cases decant the mother liquor, and recrystallize the residue from warm water.

Solutions of the "alums" have a tendency to supersaturate, and such metastable solutions may pass to complete dryness without showing individual crystals. Recrystallization must then be resorted to; sometimes several trials are necessary before characteristic octahedra are obtained.

A metastable state can usually be avoided by spreading out the test drop into a large thin drop before the cesium salt is added and then crushing the reagent in the drop immediately after it is added. As soon as alum crystals begin to form, crush one or more with a glass rod and draw the crushed material across the drop.<sup>8</sup>

Isotropic double sulphates crystallizing in octahedra are formed by elements other than aluminum, gallium, and indium, as has been dis-

<sup>6</sup> Papish and Holt: *Jour. Phys. Chem.* 32, 145 (1928).

<sup>7</sup> This method of procedure, *i.e.*, precipitation of the hydroxide and subsequent solution in the proper acid, should always be followed in *all* tests for  $\text{Al}^{+++}$ ,  $\text{Ga}^{+++}$ , and  $\text{In}^{+++}$ .

<sup>8</sup> Schoorl has suggested inoculating the test drop with a very minute fragment of cesium alum, thus "seeding" the preparation and inducing crystallization. It has also been suggested to perform the test on an object slide where a little cesium alum has previously been crystallized and carefully washed off with hot water.

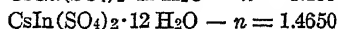
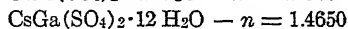
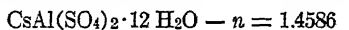
cussed on page 169. The preliminary precipitation with  $\text{NH}_4\text{OH}$  and solution of the precipitate will generally yield evidence as to the presence of these other alum-forming elements — Cr, Fe, Tl, Mn.

Although this test affords no differentiation between aluminum, gallium, and indium, the last two elements are so rare in ordinary practice that the cesium alum reaction may be considered as the most satisfactory identity test for aluminum now available. If there are reasons for suspecting that gallium or indium may be present, separate the hydroxide as outlined on page 175.

The cesium indium alum is much more soluble than the isomorphous cesium aluminum compound and is therefore not readily obtained in characteristic crystals. It is important that the indium be present as sulphate and not as chloride or bromide, since the double chloride of cesium and indium is apt to be formed instead of the double sulphate. (See page 181.) In our experience the presence of a little free  $\text{H}_2\text{SO}_4$  is desirable. These remarks relative to indium apply with equal force to gallium.

Although the "alum" test with cesium sulphate may lead to the separation of isotropic double sulphates of cesium other than those of the aluminum group, *e.g.*, those with chromium, manganese, titanium, thallium, and iron, there is no danger of confusion since all these salts are more or less colored and crystallize less readily.

It might be thought that a differentiation between the aluminum, gallium, and indium cesium alums should be possible through a determination of their refractive indices; this is not practicable, as will be seen by the following data:<sup>9</sup>



The addition of  $\text{Cs}_2\text{SO}_4$  to material of unknown composition, which has been prepared for analysis by treatment with  $\text{H}_2\text{SO}_4$ , may give rise to the separation of anisotropic double sulphates mostly to be referred to the monoclinic system. When these salts appear, they are apt to puzzle the analyst; those most frequently encountered are the cesium double sulphates of magnesium, manganese, copper, zinc, cadmium, nickel, and cobalt. Fortunately, their solubilities are higher than those of the alums and therefore they do not as a rule become troublesome, unless the concentration of salts in the test drop is too high or there has been too much  $\text{H}_2\text{SO}_4$  used. They are usually so orientated upon the object slide that an extinction angle can be measured, and, if this is done and the salt is not an isomorphous mixture, presumptive evidence of its component ions is possible.<sup>10</sup>

<sup>9</sup> For complete data on the refractive indices of the "alums," see Winchell: *Microscopic Characters of Artificial Inorganic Solid Substances or Artificial Minerals*, 2nd Ed., p. 260.

<sup>10</sup> See Winchell: *Microscopic Characters of Artificial Inorganic Solid Substance, or Artificial Minerals*.

With bismuth an almost insoluble double sulphate is formed. (See Potassium, page 71; Bismuth, page 236.)

Because of the possibility of the formation of a variety of double sulphates it is essential that a moderately large fragment of  $\text{Cs}_2\text{SO}_4$  shall always be added to the drop of solution to be tested.

The salt  $\text{CsAl}(\text{SO}_4) \cdot 12\text{H}_2\text{O}$  has, under certain conditions, marked adsorptive powers and may separate distinctly colored and in modified crystal form; this source of error can be avoided by always following the method suggested above, *i.e.*, first precipitating the hydroxide of aluminum, washing, and dissolving it in dilute  $\text{H}_2\text{SO}_4$ .

#### Experiments.

- (a) To a test drop consisting of a solution  $\text{Al}_2(\text{SO}_4)_3$  add a fragment of  $\text{Cs}_2\text{SO}_4$ .
- (b) Precipitate another drop with  $\text{NH}_4\text{OH}$ , decant, wash the precipitate, dissolve in the least possible amount of  $\text{H}_2\text{SO}_4$ , and test.
- (c) Test for Al in the presence of free HCl.
- (d) Prepare slides of chrome alum, iron alum, etc., then mixtures of these various alums; note isomorphism.
- (e) Test preparations containing Al and Fe; Al and Cr; Al, Fe, and Cr; Al in the presence of phosphates.

#### B. By Means of Ammonium Paramolybdate — $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ .

##### *Compound Formed — (?)*<sup>11</sup>

Of the various ways this test may be performed, that which has given us the most dependable results is the addition of the reagent by Method II, page 33.

The test drop should be large, neutral, or very nearly so, and must be moderately concentrated in  $\text{Al}^{+++}$ . A large fragment of clear crystalline ammonium molybdate is added to the center of the drop. When dealing with mixtures, the preparation should be gently warmed.

After standing a short time, the preparation is studied.

Aluminum forms thin, colorless, transparent plates in a zone around the reagent fragment. Very small at first, singly, with sharply defined edges, they increase rapidly in size and become foliated or granular. Preparations heated too hot yield skeletal crystals in the form of more or less opaque, four-pointed stars and clumps of foliated plates. At first sight, the well-formed plates, Fig. 94, page 135, appear to be square, but on close examination they will be seen to be rhombiform

<sup>11</sup> The true nature of the reaction products is still in doubt. This is not surprising since the formula of the reagent itself is not definitely established. According to Staples [*Amer. Mineralogist* 21, (1936)] the crystalline compound of aluminum which separates in this test is an ammonium aluminum molybdate which has either the formula  $3(\text{NH}_4)_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot x\text{H}_2\text{O}$  or  $(\text{NH}_4)_3 \cdot \text{H}_8(\text{AlMoO}_4)_6 \cdot x\text{H}_2\text{O}$ .



with the smaller angles very close to  $90^\circ$  ( $86^\circ$ , Staples). They have a high index of refraction, exhibit symmetrical extinction, and gray, white, and yellow polarization colors of the first order.

If after standing a few minutes, no crystals appear, the preparation should be warmed, thoroughly cooled, and again searched for rhombiform plates. In some mixtures several warmings may be required to produce the required equilibria. Supersaturated solutions are not uncommon.

Nickel forms crystals identical in appearance with those of aluminum; so also does iron (as  $\text{FeSO}_4$ ) and in addition, in the case of  $\text{Fe}^{++}$ , there is a brown-colored zone surrounding the reagent fragment.

Silver yields an "amorphous" heavy white precipitate but no crystals. In mixtures of silver and aluminum the heavy white precipitate is first formed interspersed in a short time with thin colorless plates, more or less foliated and shaped somewhat like an hour-glass in outline; on longer standing the characteristic typical rhomboidal plates of the aluminum compound can be easily distinguished.

With mercuric salts a granular precipitate is first formed interspersed with a few malformed crystals. Tiny, slightly elongated, thin, six-sided plates next appear and finely rectangular plates and lath-shaped prisms (Fig. 92, page 135). Extinction is slightly oblique. A very characteristic feature of this mercury complex is that between crossed nicols the largest of the rectangular plates will be found to be symmetrical fourlings (Fig. 93, page 135). In solutions containing mercury and aluminum both elements can be simultaneously identified in the same test drop. Mercury in the form of mercurous nitrate yields "amorphous" precipitates only.

$\text{Ca}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Be}^{++}$ ,  $\text{Ga}^{+++}$ ,  $\text{In}^{+++}$  appear to yield no crystalline compounds under the conditions of the test as described above. But if present in even relatively small amounts, they prevent the identification of aluminum at room temperature; on warming, a characteristic reaction for  $\text{Al}^{+++}$  is, however, obtainable in mixtures.

In the presence of cadmium a reaction for aluminum can usually be obtained at room temperature. The "amorphous" precipitate yielded by  $\text{Cd}^{++}$  does not interfere with the formation of typical plates. However, the sensitivity of the reaction for  $\text{Al}^{+++}$  is diminished. Zinc completely inhibits the reaction for  $\text{Al}^{+++}$  in the cold even if in small amount, but warmed preparations can be made to yield satisfactory tests for  $\text{Al}^{+++}$ .

$\text{Tl}^+$ ,  $\text{Cu}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Cr}^{+++}$ , all form "amorphous" precipitates only. Preparations containing these ions can be made to give reactions for  $\text{Al}^{+++}$  only when warmed and when aluminum is present in an

amount in excess of these ions. Sometimes several warmings with the addition of more water is essential, but eventually a satisfactory identification of aluminum can usually be made.

Lead as nitrate and tin as chlorostannic acid ( $\text{H}_2\text{SnCl}_6$ ) yield such dense and heavy white precipitates that the reaction for aluminum is completely inhibited. Even on warming the test fails unless these two metals are present in very small amounts only. Of the common metals, lead and tin appear to be the only ones which render the molybdate test for aluminum futile.

The most dependable reactions are obtained with chlorides and nitrates. With sulphates the reaction is retarded and is, in general, less sensitive.

The test drop should be neutral or nearly so. Free acid should be removed by careful evaporation rather than by treatment with ammonium acetate or sodium acetate since a very little excess of either of these buffer materials is likely to interfere seriously with the formation of typical crystals.

The aluminum complex is readily soluble in warm water, much less in cold. If the preparation has been warmed it should be thoroughly cooled and allowed to stand for a few minutes before being studied. Supersaturation is likely to result. Scratch the slide with glass rod or platinum wire to induce crystallization (see *Vol. I*, page 330).

The molybdate test for  $\text{Al}^{+++}$  appears to be much less sensitive than the cesium sulphate test (Method A, page 176) but the sulphate test is given by other "alum"-forming elements.

Compounds which might lead to the formation of salts of heteropoly acids must be absent.

The reagent undergoes partial hydrolysis on dissolving, does not crystallize out well from the test drop save at the periphery where it forms six-sided foliated plates and prisms with oblique extinction and very brilliant polarization colors. Though monoclinic and forming foliated plates, it cannot be confused with those of the aluminum compound.

### C. By Means of Ammonium Bifluoride — $\text{NH}_4\text{F} \cdot \text{HF}$ .

*Compound Formed* —  $(\text{NH}_4)_3\text{AlF}_6$ .

A large drop of a neutral or very slightly acid, moderately concentrated solution of the aluminum salt is placed upon a celluloid or suitably coated object slide. A large fragment of  $\text{NH}_4\text{F} \cdot \text{HF}$  is introduced into the drop and the preparation allowed to stand undisturbed for a short time. There is first formed a granular or sandy precipitate which on standing becomes distinctly crystalline; soon tiny pseudo-

octahedra, orthorhombic bipyramidal prisms, or rectangular or rhombic plates appear<sup>12</sup> (Fig. 113, page 151). The character of the precipitate varies with the concentration of the test drop with respect to  $\text{Al}^{+++}$ . If the crystals formed are atypical, it is best to decant the mother liquor (using a platinum wire, never a glass rod) and recrystallize from hot water in which  $(\text{NH}_4)_3\text{AlF}_6$  is readily soluble.

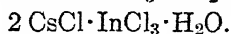
Instead of the ammonium salt the potassium salt  $\text{K}_3\text{AlF}_6$  serves equally well for the identification of aluminum and the test may be thus modified. To the concentrated solution,  $\text{KCl}$  is added and the drop stirred until all has dissolved. One or more drops of  $\text{HF}$  are added and the preparation allowed to stand, or the drop is acidified with  $\text{HCl}$ , the  $\text{KCl}$  added, and then several fragments of  $\text{NH}_4\text{F} \cdot \text{HF}$ ; or  $\text{KF}$  may be added at once in place of  $\text{NH}_4\text{F} \cdot \text{HF}$ .  $\text{RbCl}$  or  $\text{CsCl}$  can be substituted for  $\text{KCl}$ . All these salts have a composition and habit similar to ammonium fluoaluminate and form an isomorphous series. The fluoaluminates are weakly birefringent and are so feebly refractive that great care must be used in properly adjusting the illumination.

The solution to be tested should be that of a relatively pure salt of aluminum or a solution obtained by dissolving in  $\text{HCl}$  a precipitate obtained with  $\text{NH}_4\text{OH}$ .

Indium and gallium fail to give the reaction when the test is performed as described above.

#### D. By Means of Cesium Chloride — $\text{CsCl}$ .

*Compounds Formed* —  $3 \text{CsCl} \cdot \text{InCl}_3 \cdot 2 \text{H}_2\text{O}$ , or



Precipitate with  $\text{NH}_4\text{OH}$ , wash the hydroxide, and dissolve in  $\text{HCl}$ . To a moderately concentrated drop of solution thus prepared add a relatively large fragment of  $\text{CsCl}$  (or  $\text{RbCl}$ ). In a few seconds highly refractive crystals of the double salt appear. These take the form of very thin rhombs, rhombic pyramids, and rectangular prisms (Fig. 118, page 173). This salt is extraordinarily birefringent and displays very brilliant polarization colors. This property together with a characteristic habit make the double chloride test an excellent one, providing that the test is performed on comparatively pure indium (*i.e.*, upon the  $\text{HCl}$  solution of the precipitated hydroxide), for  $\text{CsCl}$  forms readily crystallizable double chlorides with the chlorides of many elements. The separation of these double chlorides may mask or interfere with the test for indium.

Aluminum tested as above gives no crystalline compound unless

<sup>12</sup> For the special precautions which are imperative when dealing with  $\text{HF}$  or its compounds, see p. 43.

the test drop passes to dryness, when a few anisotropic pseudocubic crystals may appear. If sulphates are present, aluminum alum may be precipitated.

Gallium yields a granular precipitate in which may be seen very tiny slender rods; later as the solution passes to dryness irregular anisotropic dendritic masses separate at the circumference of the drop.

Rubidium chloride may be substituted for  $\text{CsCl}$ .<sup>13</sup> The rubidium double salt is somewhat more soluble than the cesium double chloride and therefore forms larger and thicker crystals; in addition to the types described above, large, well-formed, octahedra-like crystals are obtained. These crystals are very strongly birefringent, but do not show the brilliant colors of the cesium salt. Aside from the crystals of octahedral aspect, the double rubidium salt closely resembles the cesium salt in habit.

The stability of cesium indium chloride is so great that if chlorides are present in material being tested with  $\text{Cs}_2\text{SO}_4$ , for the purpose of forming cesium indium sulphate, the former salt is apt to separate instead of the latter. A similar result follows in the case of testing with  $\text{NH}_4\text{F}\cdot\text{HF}$ ,  $\text{HCl}$ , and  $\text{CsCl}$  by Method C, page 180; the double chloride is formed and not a fluoindate.

The formula of the cesium indium chloride appears to be in doubt. It is usually given as  $\text{Cs}_3\text{InCl}_6$  or  $3\text{CsCl}\cdot\text{InCl}_3$ , but this salt appears to be tetragonal<sup>14</sup> while the salt  $2\text{CsCl}\cdot\text{InCl}_3\cdot\text{H}_2\text{O}$  is orthorhombic. Under the conditions which obtain when the test is applied as above, the salt that separates does not have a habit conforming to the tetragonal system. Moreover, the cesium salt behaves upon the object slide as if it were isomorphous with potassium indium chloride, whose formula is quite well established as being  $2\text{KCl}\cdot\text{InCl}_3\cdot\text{H}_2\text{O}$ . If the test drop is moderately concentrated with respect to indium, the crystals which separate are as described above, but if quite dilute or too concentrated other salts are formed.<sup>15</sup>

**E. By Means of Hexamethylenetetramine** —  $\text{C}_6\text{H}_{12}\text{N}_4$ . — The hydroxides prepared as directed on page 175, are dissolved in  $\text{HCl}$  with the acid in slight excess. To the test drop thus prepared add the

<sup>13</sup> Kley: *Chem. Ztg.* 25, 563 (1901).

Behrens-Kley: *Mikrochem. Anal.*, p. 82.

<sup>14</sup> Wallace: *Zeit. Kryst.* 49, 417 (1911).

Pratt: *Amer. Jour. Sci.* (3) 49, 397 (1895).

<sup>15</sup> Investigations carried out by Chamot and Cole (1923) supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.



FIG. 120. Thallium ( $Tl^+$ ) with Uranyl Acetate. 50 $\times$ .

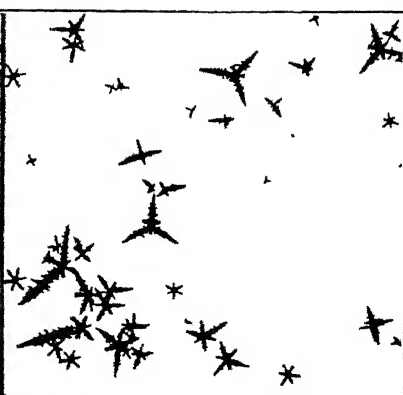


FIG. 121. Thallium ( $Tl^+$ ) with Hydrochloric Acid. 100 $\times$ .

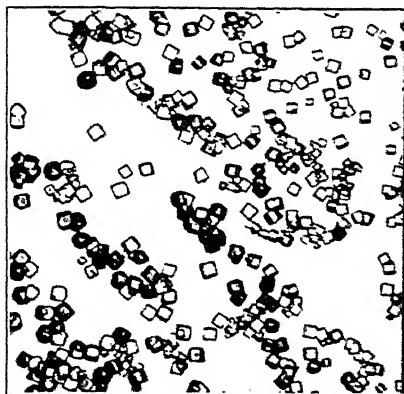


FIG. 122. Tin ( $Sn^{++++}$ ) with Cesium Chloride. 200 $\times$ .

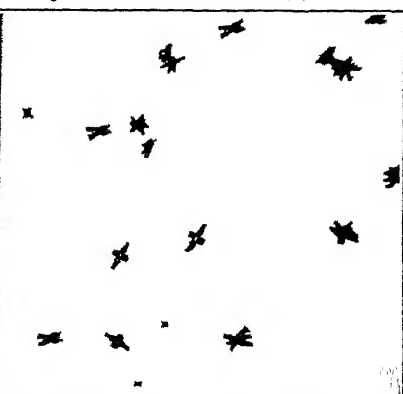


FIG. 123. Lead Sulphate Recrystallized from Conc. Sulphuric Acid. 300 $\times$ .

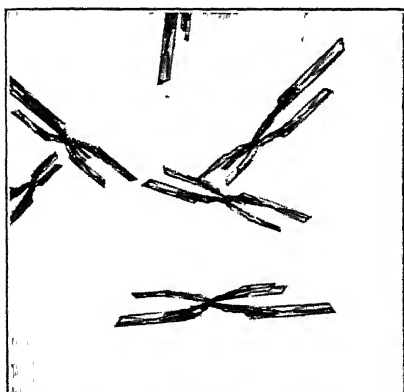


FIG. 124. Lead with Hydrochloric Acid. 100 $\times$ .

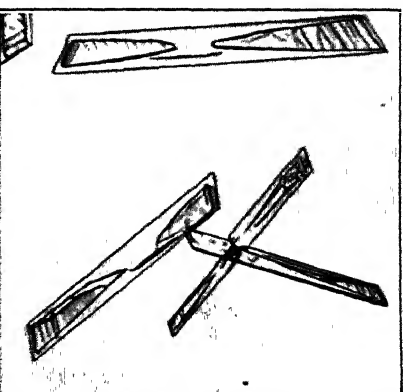


FIG. 125. Lead Chloride Recrystallized from Hot Water. 200 $\times$ .

reagent by Method II, page 33. Indium yields tiny, highly refractive, isotropic octahedra (Fig. 119, page 173). Aluminum and gallium give no crystalline precipitates with  $C_6H_{12}N_4$ .<sup>16</sup> (See page 393.)

**F. By Means of Diphenyl Carbazide.** (See page 133.)

### DETECTION OF THALLIUM

The chief properties of thallium have been discussed on page 170 in relation to its position in Group III of the Periodic System. In aqueous solutions which have been boiled, thallic compounds are changed to thallic salts; hence the analytical behavior of the latter alone need concern us.

**A. By Means of Hydrochloric Acid — HCl.**

*Compound Formed* —  $TlCl$ .

The method of procedure, characteristics, and precautions relative to the identification by means of  $TlCl$  have been discussed under Mercury, Method B, page 156. (See Fig. 121, page 183.) Confirm by treating the precipitate (1) with  $KI$  — no yellow hexagonal plates; (2) with  $H_2SO_4$  — no conversion into an insoluble sulphate (distinction from lead).

**B. By Means of Chloroplatinic Acid —  $H_2PtCl_6$ .**

*Compound Formed* —  $Tl_2PtCl_6$ .

See Potassium, Method A, page 66. If a precipitate is obtained, confirm by testing a new portion of the substance with sodium iodide.

**C. By Means of Sodium Iodide —  $NaI$ .**

*Compound Formed* —  $TlI$ .

See Mercury, Method B, page 157; Method C, page 159.

**D. By Means of the Triple Nitrite Reaction.**

*Compound Formed* —  $2 TlNO_2 \cdot Cu(NO_2)_2 \cdot Pb(NO_2)_2$ .

For a discussion of this reaction and its application to the detection of thallium, see Lead, Method C, page 207.

**E. Miscellaneous Reactions of Thallium.**

(a) Metallic zinc precipitates metallic thallium.

(b) Not precipitated by alkali hydroxides or carbonates.

(c) In dilute solutions no precipitate with  $H_2SO_4$ .

<sup>16</sup> Chamot and Cole, Heckscher Research Grant, 1923, *op. cit.*  
Martini: *Mikrochemie* 6, 28 (1928).

(d)  $\text{K}_2\text{CrO}_4$  precipitates  $\text{Tl}_2\text{CrO}_4$ , insoluble in dilute  $\text{HNO}_3$  and in dilute  $\text{H}_2\text{SO}_4$ .

(e)  $\text{TlI}$  is only very slightly soluble in excess of  $\text{NaI}$  or  $\text{KI}$ .

(f)  $\text{K}_4\text{Fe}(\text{CN})_6$  — yellow sandy precipitate.

(g)  $\text{Na}_3\text{Co}(\text{NO}_2)_6$  — fine granular or cubic precipitate.

(h) Phosphomolybdic acid, fine yellow precipitate.

(i)  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ , dense white granular precipitate, soon changing into moss-like masses and beautiful radiating clusters and sheaves of fine acicular crystals. Later hexagonal plates, six-pointed stars, and six-pointed rosettes are formed.

(j) Uranyl acetate gives tetragonal needles and prisms. (See Sodium, page 54. Fig. 120, page 183.)

For additional tests and separation methods, see Munch and Ward: *Jour. Amer. Pharm. Assoc.* 24, 351, (1935); Benedetti-Pichler and Spikes: *Mikrochemie* 9, 239 (1936).

## CHAPTER VI

### DETECTION OF THE ELEMENTS OF GROUP IV

C; Ti, Zr, Hf, Th; Si, Ge, Sn, Pb

Group IV comprises the transitional element carbon; the primary vertical subgroup, titanium, zirconium, hafnium, and thorium; and the secondary subgroup, silicon, germanium, tin, and lead.

Carbon has no microanalytical relations with the other elements of Group IV. We have no satisfactory "micro" reactions for carbon and we can test for its presence only indirectly through its oxide  $\text{CO}_2$  fixed in carbonates.

Titanium and zirconium (hafnium) are closely related, not only as to the compounds they form but also in their behavior toward micro-analytical reagents; none of their "micro" reactions however, are similar to those of thorium.

Both titanium and zirconium are acid-forming and we therefore encounter titanates and zirconates in materials whose qualitative analyses are required, rather than compounds in which titanium or zirconium functions as cations; but the detection of the elements titanium or zirconium is required in alloys, pigments, refractories, and in minerals.

The compounds of titanium with which the analyst is ordinarily concerned are derivatives of tetravalent titanium, less often of trivalent titanium. Also in the case of zirconium it is with derivatives of the oxide  $\text{ZrO}_2$  that he has to deal. Most compounds of titanium in which this element plays the part of a cation are very unstable and hydrolyze readily; the same is true of salts of zirconium but to a less degree. The most stable simple salt of zirconium is  $\text{Zr}(\text{NO}_3)_4$ .

White  $\text{TiO}_2$  is readily differentiated from white  $\text{ZrO}_2$  by heating.  $\text{TiO}_2$  turns yellow while hot, white again on cooling;  $\text{ZrO}_2$  undergoes no change of color on heating.

Titanium in  $\text{HCl}$  solution behaves somewhat like  $\text{SnCl}_4$  but is more readily hydrolyzed on boiling. Zirconium, being more basic, its salts are slightly more stable, but most simple zirconates are decomposed by water in the cold. The resemblance of titanium and zirconium to silicon and tin is shown by the formation of the oxides  $\text{TiO}_2$  and  $\text{ZrO}_2$ , the ease with which they dissolve in  $\text{HF}$ , and their formation of the



acids  $\text{H}_2\text{TiF}_6$  and  $\text{H}_2\text{ZrF}_6$  which closely resemble in their reactions the reactions of  $\text{H}_2\text{SiF}_6$ . But their dioxides, unlike  $\text{SiO}_2$ , are soluble in concentrated  $\text{H}_2\text{SO}_4$ , with the formation of sulphates.

Further analogies of titanium to silicon and to tin are the formation of the acid  $\text{H}_4\text{TiO}_4$  (or  $\text{Ti}(\text{OH})_4$ ) and the readiness with which titanium forms polyacids. However, most titanates have the formula  $M^{++}\text{TiO}_3$  (corresponding to salts of a meta-acid), or  $M^{++}\text{Ti}_2\text{O}_5$ .

The alkali salts of  $\text{H}_2\text{TiF}_6$  and  $\text{H}_2\text{SiF}_6$  are isomorphous, and it is probable that the alkali salts of  $\text{H}_2\text{ZrF}_6$  are also isomorphous with the fluo-acids of silicon and titanium.

Solutions of the alkali titanates and zirconates are unstable, hydrolyze slowly on standing, and are decomposed on boiling.

For the detection of titanium, zirconium, silicon, and germanium, we are almost wholly dependent upon the formation of crystalline salts of the alkalis and alkaline earths with the fluo-acids of these elements.

In both the vertical subgroups of Group IV the basicity increases with the rise in atomic weight. Thus carbon and silicon at the top of the groups are strictly acid formers (metalloids), whereas in hafnium and thorium, and in tin and lead, the acidic properties are submerged in the strong basicity of these metals. Hafnium and thorium are better classed with the "rare earths"; therefore their separations and detections are best discussed in connection with the other "rare earths." (See pages 308–313.)

The micro detection of silicon, like that of carbon, is impractical unless there is first conversion into its oxide, and subsequently the formation of an acid is induced. The ease with which  $\text{SiO}_2$  is converted into  $\text{H}_2\text{SiF}_6$  affords a simple and satisfactory test for silicon and silicates providing that titanium, zirconium, germanium, or tin is absent.

Germanium reacts like silicon in forming fluogermanates, and like phosphorus and arsenic in forming volatile chlorides. A further resemblance to these elements is seen in the formation of complex heteropolyacids.

Tin and lead have nothing in common microanalytically, nor do they appear with any of the reaction products which serve to identify the other members of Group IV, save that tin forms crystalline stannates and fluostannates. (See page 65.) Their analogies are rather with adjacent elements in the horizontal periods but not with those above them. These analogies and differences hold true for all the heavy metals of highest atomic weight in the vertical columns of the eight groups of the Periodic System of the elements. Like these other elements of high atomic weight, both tin and lead form two series of salts, "ous" and "ic."

Hafnium resembles zirconium so closely that it cannot at present positively be identified, nor differentiated from zirconium by microcrystalline reactions alone. Thorium's reactions place it with the "rare earths."

### DETECTION OF CARBON

The microscopical detection of carbon is ordinarily confined to the examination of commercial products in which carbon may be a component (a) in natural or synthetic organic compounds; (b) in black or dark-colored pigments; (c) black material in specks or fragments in, or upon, the surfaces of products which should be free from such specks.

In the first of these groups the detection is based upon the oxidation of the carbon to carbon dioxide in a current of air or of oxygen in a tiny combustion tube, absorption of the  $\text{CO}_2$  in alkali, and testing for the presence of carbonates as outlined on page 323. Or the material may be treated by any one of the "combustion" methods employed in qualitative organic analysis.<sup>1</sup>

In the second group — black pigments — the most common materials are:

Carbon (gas) Black	Both "amorphous," very finely divided, with tendency toward agglomeration. Volatile on ignition, leaving little or no ash. Microscopical appearances different from other black pigments.
Lamp (oil) Black	
Bone Blacks (Ivory, Drop, Coach Blacks)	Largely volatile on ignition, but leaving ash high in calcium phosphate. Usually a characteristic odor on ignition. Particles vary in size. In larger particles cellular structure of bone discernible.
Mineral Blacks	Non-carbonaceous, ground black stony material such as black slates, non-volatile, particles very variable in size, siliceous.
Vegetable Blacks	Charcoals, from calcination of compact vegetable tissue, leave an appreciable ash, particle size variable. Larger particles show cellular structure characteristic of their origin.
Aniline Blacks	Definite organic compounds, very finely divided, almost completely volatile. May be soluble in organic or inorganic solvents. Microscopical appearances not characteristic. If salts of inorganic substances, ash is high.
Asphalts, Bitumens, Tars, etc.	Most of these products completely soluble, or nearly so, in organic solvents. Odors usually characteristic on heating. Melt on warming.

<sup>1</sup> Emich: *Mikrochemisches Praktikum* (Bergmann, München, 1931). Pregl: *Die quant. organ. Mikroanalyse* (Springer, Berlin, 1930). Pregl-Roth-Daw: *Quantitative Organic Microanalysis* (Blakiston, Philadelphia, 1937). Emich-Schneider: *Microchemical Laboratory Manual* (Wiley, New York, 1932).

In the third group of materials of a carbonaceous nature likely to be the cause of specks and stains, in addition to any one or more of those listed above, there must be taken into account—graphite, coal, coke, partly carbonized lubricating oils and greases; crushed, dark-colored insects, etc.

Graphite is commonly met with as soft, dense, brown, gray or black “amorphous” matter or in the form of glistening micaceous scales or flakes, often iridescent; rarely it occurs in black, six-sided plates and tablets. It is sometimes encountered in the cooler regions of certain types of high-temperature furnaces which are gas heated; particularly when chlorides are present.

Graphite does not ash readily, leaving little or much ash, depending upon its purity. It does not dissolve in concentrated acids or alkalis, nor is it appreciably attacked by alkali carbonate or pyrosulphate fusing mixtures. Graphite is not attracted by a magnet, a differentiation from magnetite ( $\text{Fe}_3\text{O}_4$ ), with which it has often been confused.

Graphite cautiously heated with a mixture of nitric acid and potassium chlorate yields a yellowish crystalline material which has been called “graphitic acid,” whereas “amorphous carbon” is oxidized to  $\text{CO}_2$  by this reagent mixture (Brody's Reaction).

The identification of carbides (or of carbon thus combined) must depend upon the identification of the products of decomposition. Practically, each carbide constitutes a special case, and the plan of attack must be formulated in accordance with the chemical reactions which may be brought about with a variety of reagents. The problem is difficult of solution. No microscopical methods of general applicability are possible.

### DETECTION OF SILICON, GERMANIUM, TITANIUM, AND ZIRCONIUM

With the exception of zirconium the micro reactions of this group of elements are so nearly identical that their differentiation on a “micro” scale is often impracticable.

The hope of positive identification must be based upon separation methods before an identity test can be successfully applied. Some of the separation methods which offer a possible chance of success are discussed below, following the special reactions. (See pages 199, 200.)

The analyst is commonly faced with a further difficulty in that he must detect Ti, Zr, and Si in the presence of each other and in the presence of large amounts of other elements, as, for example, in alloy steels. The preliminary concentrative operations cannot therefore all be performed upon object slides but must involve weights and volumes many times greater than those required in strictly “micro” methods.

**A. Conversion into Alkali Salts of Fluo-acids —  $H_2RF_6$ .**

*Compounds Formed* —  $Na_2SiF_6$   
 $Na_2GeF_6$   
 $Rb_2TiF_6$   
 $Rb_3ZrF_7$ .

Use a celluloid, cellulose acetate, or other non-siliceous, transparent, object slide and observe all the precautions given on page 43.

To a concentrated drop somewhat larger than is usually employed in microchemical analysis add a tiny droplet of dilute  $H_2SO_4$ , then a fragment of  $NaCl$ . Stir with a platinum wire and add a large fragment of resublimed  $NH_4F \cdot HF$ . Warm the preparation by laying it upon a warm metal surface. (See Fig. 1, page 5.) Allow to stand for a few minutes until thoroughly cold and crystals have begun to form.

Warming the preparation is not essential but is nevertheless advisable, for it accelerates the reaction and appears to prevent or at least greatly retard the formation of the acid fluoride of sodium  $NaF \cdot HF$ , which crystallizes in six-pointed rosettes and six-sided plates and prisms. The salt  $NH_4F \cdot HF$  forms pseudotetragonal or pseudocubic (orthorhombic, Winchell) tablets and prisms.

Instead of using the ammonium fluorides, Staples<sup>2</sup> believes it to be better and more convenient to use  $NaCl$ ,  $CaF_2$ , and  $H_2SO_4$ . This avoids the necessity of purifying the ammonium bifluoride by sublimation and also of keeping the fluoride in hard rubber vials.

Many analysts prefer the use of hydrofluoric acid instead of fluorides as it reduces the number of cations in the final preparation and the danger of contaminated fluorides.

When  $HF$  is used, Rochow<sup>3</sup> has pointed out that in the case of silicon when  $HF$  is added to the test drop *before* the sodium salt, prisms of the fluosilicate predominate; but, if it is added *after* the sodium, basal pinacoids predominate.

All four elements yield rosettes, six-sided plates, skeletons of hexagons, perfect hexagons, and six-sided prisms with square ends or terminating in pyramids (hexagonal system). Their indices of refraction are all so very low that they are almost invisible ( $n \approx 1.31+$ ; water  $n = 1.33+$ ). Their birefringence is also very low.

$Na_2SiF_6$  and  $Na_2GeF_6$  are isomorphous and of sufficiently low solubility to separate before the test drop has evaporated to dryness; the colorless crystals appear pink under the microscope (Christiansen effect), and separate first at the circumference of the drop. (See

<sup>2</sup> *Amer. Mineralogist* 21, 379 (1936).

<sup>3</sup> Personal communication, 1938.

Sodium, page 62.)  $K_2SiF_6$  is quite soluble but  $K_2GeF_6$  is very difficultly soluble and separates in colorless, thin, hexagonal plates and tablets which exhibit the Christiansen effect.  $K_2TiF_6$  separates in very thin scales and in four-sided and six-sided plates (hexagonal ?); rarely in four-sided tablets. Under unusual conditions the crystals may have a pseudo-octahedral aspect, resembling the corresponding zirconium compound but having a lower index of refraction.

The solubilities of  $Na_2TiF_6$  and  $Na_2ZrF_6$  are too great for these salts to separate unless the concentration is very high and the test drop is about to pass to dryness.

Since the silicon and the germanium salts have a sufficiently low solubility to appear in crystal form after the preparation has stood several minutes, the non-appearance of pink hexagons indicates the absence of silicon and germanium. To the preparation there can then be added  $RbCl$ ; if titanium is present, thin, square and rectangular plates with truncated corners, rhombs, and six-sided plates (not regular hexagons) of the compound  $Rb_2TiF_6 \cdot 2H_2O$  are obtained.

Zirconium yields a mass of fine granular crystals and highly refractive isometric octahedra having the composition  $Rb_3ZrF_7$  (Fig. 117, page 173). Usually six-sided plates and tablets are also present. The concentration of Zr ions must be relatively high and the preparation must stand a few minutes to allow full development of characteristic crystals. The potassium fluozirconates are somewhat more soluble and vary in composition with concentration.  $K_2ZrF_6$  separates in monoclinic, strongly birefringent prisms but is not likely to be formed in normal test drops, as there will always (?) be present a sufficient excess of  $KF$  to form the isometric salt  $K_3ZrF_7$ .

Boron must be absent since it forms with sodium and fluorine  $Na_2BF_6$  identical in appearance and isomorphous with  $Na_2SiF_6$  and  $Na_2GeF_6$  (Figs. 37, 38, page 61). The fact that the fluoborate usually does not show the Christiansen effect is not sufficient ground for differentiation. The specific test for boron with turmeric-viscose-rayon fibers must always be made. (See Boron, page 170.) Titanium gives a brown color and zirconium a reddish-brown or pink, but only with boron is the fiber turned blue with  $KOH$ . Thorium gives no color. With potassium, rubidium, or cesium, the orthorhombic salts formed have the compositions  $(K, Rb, \text{ or } Cs)_2BF_4$ , all quite different in appearance from potassium fluotitanate and potassium fluozirconate. (See Boron, page 171; Aluminum, page 180.)

Since silicon and germanium are readily separated from titanium and zirconium, the  $NH_4F \cdot HF$ , or better the  $KF$ , test can be made to yield dependable results since potassium fluogermanate is very difficultly

soluble; but, if applied to material directly, the reaction becomes a general one, to be regarded merely as an indication of a group of closely related, anion-forming elements.

**B. Conversion into Complex Molybdates.**—The material to be tested is treated upon platinum foil or in a platinum cup in the manner described below. After the final treatment and evaporation to dryness on platinum, the residue is dissolved in pure water and a fragment of ammonium molybdate is added. The mixture is next heated to boiling to ensure the formation of the necessary complex molybdates. Evaporate again almost to dryness, treat with  $\text{HNO}_3$ , and once more evaporate. Dissolve the residue in a drop or two of pure water and transfer the very dilute solution to a celluloid object slide. Add to the *clear* solution a fragment of  $\text{RbCl}$ .

Rubidium silico-molybdate or rubidium germano-molybdate is formed. Both these compounds separate with identical habit—tiny, isotropic, yellow globular crystals or octahedra and dodecahedra. (See page 83; Fig. 48, page 77.)

Freshly distilled water should be employed, not water that has stood for a long time in glass.

It is obvious that evaporation cannot be performed on glass or quartz object slides, nor in glass, quartz, or porcelain vessels, nor can the final observations be made upon a glass or silica object slide unless protected by a suitable varnish.

The test is sensitive to very minute amounts of silicon or germanium, hence it is essential that a "blank" be carried out with all the materials employed.

Somewhat better crystals of rubidium silico- or germano-molybdate can usually be obtained by applying the tests as suggested under rubidium and cesium.

If rubidium and cesium (and  $\text{Tl}^+$ ) are absent and a very fine yellow precipitate appears on heating a test drop of a water solution with  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in  $\text{HNO}_3$ , compounds of phosphorus or arsenic are probably present (i.e., ammonium phospho-molybdate or ammonium arseno-molybdate has separated). But unless the concentration of the drop has been made too great, neither silico-molybdates nor germano-molybdates will separate until the rubidium salt has been added. Even the potassium salt of these two complex acids will not separate from dilute solutions. Behrens<sup>4</sup> has pointed out that advantage can be taken of this fact to differentiate between silicon (and Ge) and

<sup>4</sup> *Anleit. mikrochem. Anal.*, p. 95.

Behrens-Kley: *Mikrochemische Analyse*, p. 108.

vanadium, columbium, tantalum, bismuth, and also zirconium, titanium, and tin. But if thorium is present, a thorium molybdenum complex may be formed which may have an appearance not distinguishable from the silicon or germanium complexes, save that it is colorless.

In order to differentiate between Si and Ge, it is necessary to have recourse to separation methods. One of the simplest of these is that of distilling off the  $\text{GeCl}_4$  in the presence of concentrated HCl. The solution to be tested is evaporated to dryness at a temperature not over  $75^\circ \text{C}$ . in a micro crucible (Fig. 10, page 17). To the residue several drops of concentrated HCl are added and sufficient asbestos fibers to prevent spirting. The crucible thus prepared is covered with a celluloid or other non-siliceous object slide and heated gently.  $\text{GeCl}_4$  distills at  $86^\circ \text{C}$ .<sup>5</sup> As soon as vapors condense upon the cover slide, discontinue the heating; allow to stand a few seconds and heat again. Repeat the process several times until the condensate upon the slide is as large in amount as the slide will carry. Remove the slide, replace it by a fresh one, and distil again. Unite all the distillates, transfer to a platinum cup or foil, acidify with  $\text{HNO}_3$ , add  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ , and proceed as above. Germanium, however, cannot be separated from completely dehydrated  $\text{SiO}_2$  residues by distillation.

Arsenic may have passed over with the germanium;<sup>6</sup> therefore it is wise to test the distillate with  $\text{NH}_4\text{F} \cdot \text{HF}$  and KCl as well as with  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$  and RbCl.

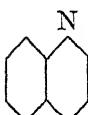
In order to eliminate as far as possible such other elements as may give products similar to rubidium silicomolybdate it is best to separate the silicon from the other material. Fuse the material in a platinum cup with several times its weight of  $\text{Na}_2\text{CO}_3$ . Dissolve in HCl, evaporate to dryness, and heat the residue (but not above  $110^\circ \text{C}$ .). Moisten with concentrated HCl and heat again; repeat the process so as to render the  $\text{SiO}_2$  insoluble. Extract the residue repeatedly with dilute HCl, filtering if necessary to avoid loss of  $\text{SiO}_2$ . Dry the  $\text{SiO}_2$  and fuse with  $\text{Na}_2\text{CO}_3$ . Dissolve in water, add the molybdate, and proceed as directed above.

The residue of insoluble  $\text{SiO}_2$  may contain germanium, titanium, columbium, tantalum, and adsorbed traces of other oxides. The absence of molybdate-forming elements always must be proved before the presence of silicon can be considered as assured. Checks should be

<sup>5</sup> Dennis and Hance: *Jour. Amer. Chem. Soc.* 44, 305 (1922).

<sup>6</sup> The boiling points of the volatile chlorides which may be thus separated from interfering compounds in microscopical analysis are:  $\text{GeCl}_4$   $86.5^\circ$ ;  $\text{AsCl}_3$   $130^\circ$ ;  $\text{SbCl}_3$   $220^\circ$ ;  $\text{HgCl}_2$   $304^\circ$ ;  $\text{SeOCl}_2$   $176^\circ$ .

made by carefully volatilizing the silicon as  $\text{SiF}_4$  and testing the residue with  $\text{KF}$ .

C. By Means of Quinoline —  — and Ammonium Thiocyanate,  $\text{NH}_4(\text{SCN})$ .<sup>7</sup>

*Compounds Formed* — (?)

In performing this test for differentiating between Ti, Zr, Va, U, Mo, and W the material should be present as chlorides (less satisfactory as nitrates). The test drop must be strongly acid to prevent hydrolysis.

*Quinoline Reagent* — Quinoline, 6 drops; concentrated  $\text{HCl}$ , 4 drops; mix thoroughly and add 4 drops of water. Mix until a clear liquid of uniform concentration is obtained.

*Ammonium Thiocyanate* — Saturated solution in water.

*Test Drop* — A large drop of  $\text{HCl}$  (1 : 2) in which the material to be tested is dissolved to a clear solution. Moderate concentrations are essential.

To the test drop add a small drop (not quite one half the size of the test drop) of the quinoline reagent. Stir very thoroughly so as to mix the reagent uniformly with the test drop. This step is essential. No precipitation should result. If a precipitate, crystalline or otherwise, is formed, the cause of this phenomenon must be ascertained before proceeding with the test (see below).

Into the clear quinoline-containing test drop, cause to flow by Method I, page 31, a saturated solution of ammonium thiocyanate. A colorless (white) or colored precipitate is formed consisting of oily droplets. Set the preparation aside for a minute or two undisturbed in order to permit crystallization of the metal complex. If no crystallization of the oil takes place, stir the preparation. Metastable conditions commonly prevail. The preparation, however, must be studied before it passes to dryness and also before the huge isotropic dendrites of ammonium chloride (formed by the action of the  $\text{HCl}$  on  $\text{NH}_4(\text{SCN})$ ) completely fill the drop.

Titanium yields an emulsion of yellow or orange oil. Eventually the droplets coalesce and crystals make their appearance in the form of small, thin, yellow disks, scales, elongated hexagons, short, stout, deep yellow, highly refractive and dispersive prisms (Fig. 126, page 195) or dendritic masses. Not infrequently the six-sided plates and prisms do not develop properly but appear as rods. When rapidly formed, skeleton and dendritic crystallites predominate and the very charac-

<sup>7</sup> Martini: *Trabajos al Segundo Cong. de Química, Buenos Aires, 1924.*



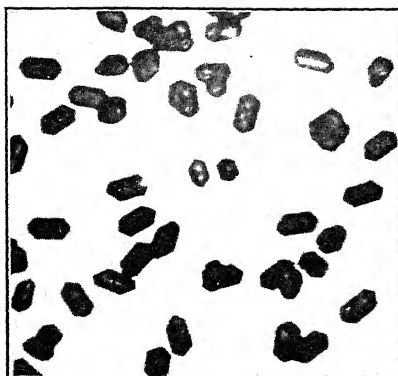


FIG. 126. Titanium with Quinoline and Ammonium Thiocyanate. 150X.



FIG. 127. Titanium with Quinoline and Ammonium Thiocyanate. 70X.



FIG. 128. Zirconium with Quinoline and Ammonium Thiocyanate. 100X.



FIG. 129. Zirconium with Quinoline and Ammonium Thiocyanate. 70X.

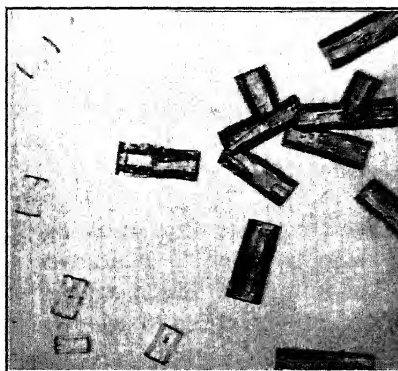


FIG. 130. Uranium with Quinoline and Ammonium Thiocyanate. 150X.



FIG. 131. Uranium with Quinoline and Ammonium Thiocyanate. 70X.

teristic six-sided plates and prisms are masked by the overgrowth of dendrites. Preparations should always be searched for these plates, prisms, or rods, since these appear to be specific for titanium. If only dendrites are seen (Fig. 127, page 195), several preparations should be tested, varying the concentrations.

Zirconium yields a white precipitate (emulsion of colorless oily drops), and in a short time colorless, imperfect rosettes composed of thin scales and plates; skeleton crystals are always present (Figs. 128, 129, page 195). When titanium is present the rosettes of the zirconium complex are colored, the intensity of the yellow or light orange depending upon the relative amount of Ti in the test drop. Crystals of the titanium complex may often be found.

Vanadium first yields a white (colorless) oily emulsion which slowly turns yellow. A rather high concentration of vanadium is essential in order to obtain crystals without "seeding" or other means of overcoming a persistent supersaturation. When other methods fail, warming very gently should be tried. Well-formed, discrete crystals are seldom obtainable. Ordinarily the precipitate consists of an aggregation of colorless, thin blades and plates, sometimes tablets and prisms. These aggregates are usually asymmetrical radiates or have the appearance of imperfect "bow-knots" (Fig. 132, page 197). When the component crystals of the aggregates are very slender the mass appears to be brown in color. Very small amounts of iron color the crystals pink, the intensity of the color increasing with the increase of iron content until a sufficient quantity is present to give rise to the formation of deep-red plates of the iron complex.<sup>8</sup>

Iron yields a deep red solution, an emulsion of deep red, oily drops, and eventually garnet-red dendrites or rectangular, three-sided, six-sided, or rhomboidal plates and tablets. Single crystals are few in number; clumps of overlapping plates and dendritic masses predominate. Elongated plates exhibit parallel extinction and glow fire red (Fig. 135, page 197). Thick crystals are opaque and black by transmitted light. Elongated dendrites are coarsely saw-toothed owing to the overlapping triangular plates. In the absence of other cations, this test for iron is fairly sensitive.

Uranium yields an instantaneous dense, yellow, oily emulsion like that obtained with titanium, but the crystals which form at once are very different from those of the titanium complex. The characteristic crystals of the uranium complex are rectangular plates and prisms, light

<sup>8</sup> According to Martini: *op. cit.*, vanadium nitrate forms under certain conditions of concentration, and sequence of reagents, in nitric acid test drops, rhomboidal, bright-red plates.

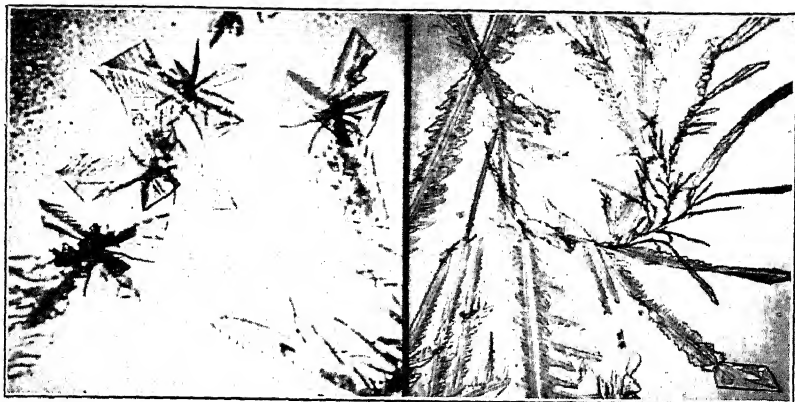


FIG. 132. Vanadium with Quinoline and Ammonium Thiocyanate. 150 $\times$ .

FIG. 133. Cobalt with Quinoline and Ammonium Thiocyanate. 70 $\times$ .



FIG. 134. Molybdenum with Quinoline and Ammonium Thiocyanate. 200 $\times$ .

FIG. 135. Iron with Quinoline and Ammonium Thiocyanate. 100 $\times$ .

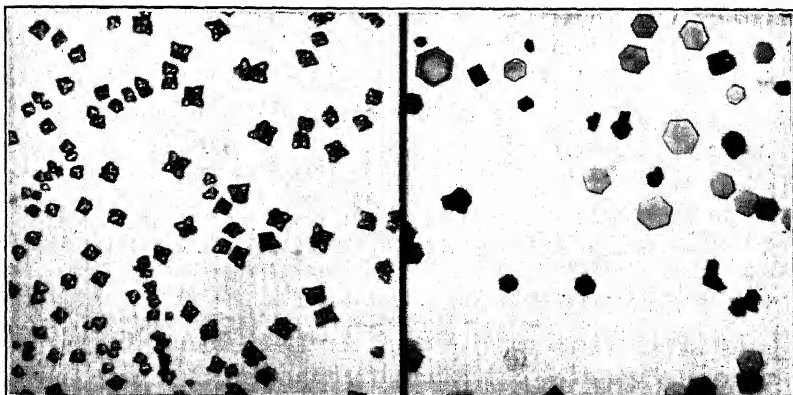


FIG. 136. Arsenic with Ammonium Molybdate. 200 $\times$ .

FIG. 137. Arsenic with Cesium Chloride and Potassium Iodide. 200 $\times$ .

yellow in color (Fig. 130, page 195), and long, thin, lath-like plates. They exhibit parallel extinction, first order colors, and are very strongly dichroic, colorless when their direction of elongation is parallel with the plane of vibration of the polarizer, yellow when at right angles thereto. In a very short time the laths assume large dimensions and large dendritic masses are formed (Fig. 131, page 195). Sheaves of long delicate needles are sometimes present. Small drops of quinoline reagent favor the formation of the small plates and prisms; large drops, dendrites and needles.

Rectangular plates and prisms strongly dichroic appear to be specific for uranium when the test is performed as described above.

Cobalt forms light blue dendrites and clumps of thin blue blades and plates derived from a heavy precipitate of blue oily drops. Metastable conditions appear to be the rule, especially when the drop of quinoline reagent is relatively large (Fig. 133, page 197).

Both nickel and copper yield dark-colored emulsions which seldom crystallize under the conditions of the test and before passing to dryness. If a few crystallites separate, they are dendritic masses of very fine needles, either somewhat feathery or in the form of disks of indeterminate color by transmitted light.

Molybdenum (as oxide or "neutral" molybdates) in HCl (1 : 2) test drops commonly fails to yield any definite reaction, the preparation passing to dryness before the emulsion of reddish oil can be induced to crystallize. However, under certain obscure conditions, small, dark red (opaque) dendrites are formed (Fig. 134, page 197).

Antimony and bismuth are immediately precipitated by the quinoline reagent. These elements must therefore be absent from materials to be subjected to the quinoline-thiocyanate reaction. The precipitate is an amorphous white solid.

Al, As, Cd, Cb, Cr, Ge, In, Mn, (Mo), Sn, Ta, W, and Zn yield no distinctly discernible crystalline precipitates when the reagents are applied in the manner and relative concentrations described.

In the case of certain salts, the addition of the quinoline reagent and stirring of the test drop (before the application of the thiocyanate) cause the precipitation of relatively large, well-formed tablets and prisms. The elements which best exhibit these phenomena are Mn, Cd, Sn, Hg.

#### **D. By Means of *n*-Propyl Arsonic Acid — $C_3H_7AsO(OH)_2$ .**

*Compound Formed* — Not definitely established.

In order to avoid hydrolysis it is essential that the test drop containing chlorides of the materials to be tested shall be strongly acid

We have found it best to acidulate the aqueous test drop with an equal volume of HCl (1 : 2) unless the acidity of the solution in question is known to have a pH of approximately this final acidity. To the test drop thus prepared, add a dry fragment of the arsonic acid reagent (Method II, page 33).

If zirconium is present, there should result an immediate white precipitate in an expanding zone around the reagent fragment. Under the microscope this precipitate is "amorphous." No crystals are formed. Although such a precipitate is not in accord with good microscopical identification tests, an exception must be made, since in this particular case the formation of a precipitate (any precipitate) is strictly specific for zirconium. (For further details, see Separation Methods below.)

#### Procedures in Brief for the Qualitative Separations of Ti, Zr, Cb, Ta, U, Mo, V

These suggested methods, in mere outline, assume that the analyst shall have made preliminary partial separations whereby some of the elements present have been eliminated.

(a) *Zirconium from other elements.*<sup>9</sup> The solution should be in the form of chlorides in strong HCl. Silica is removed by evaporation with HCl in the usual manner. Cb, Ta, W, and small amounts of Ti and Zr are co-precipitated with the silica, but the bulk of Zr, Ti, and all the U, Mo, and V pass into solution in the HCl extract. This extract is made strongly acid with HCl and to it is added a 5 per cent solution of *n*-propyl arsonic acid,  $C_3H_7AsO(OH)_2$ . Heat to boiling. Zirconium propyl arsonate, alone, is precipitated. Centrifuge or filter, wash, dry, and ignite;  $ZrO_2$  is obtained. Confirm, if desired, by other tests.

The following elements do not yield precipitates nor do they interfere with the test: Al, Ba, Be, Ca, Cd, Ce, Co, Cb, Cu, Ge, In, Ir, Fe, Li, Mg, Mn, Hg, Mo, Ni, Pd, Pt, Rh, Sr, Ta, Th, Sn, Ti, U, V, W, Zn. We have carefully checked all these elements and confirm the statement made by Arnold and Chandlee that this precipitation appears to be strictly specific for zirconium. Although it is reported that Sb and Bi must be absent when this reagent is used for the quantitative determination of Zr, neither of these elements appears materially to affect the reaction as described under Method D, page 198.

(b) *Zirconium, columbium, and tantalum from Ti, U, Mo, W, V, by means of disodium phosphate in strong HCl solution.* Add to the

<sup>9</sup> Arnold and Chandlee: *Jour. Amer. Chem. Soc.* 57, 8 (1935).

HCl solution  $\text{H}_2\text{O}_2$  and then a solution of the phosphate. Warm gently. Test for complete precipitation. Centrifuge or filter. Zr, Cb, and Ta are precipitated as phosphates. The filtrate will contain Ti, U, Mo, W, V, and some Cb and Ta. If Zr is absent, Cb and Ta are not precipitated. Ti remains in solution only when  $\text{H}_2\text{O}_2$  has been added.<sup>10</sup>

(c) *Titanium from salts of  $\text{Al}^{+++}$ ,  $\text{CrO}_4^{--}$ ,  $\text{WO}_4^{--}$ ,  $\text{MoO}_4^{--}$ ,  $\text{UO}_2^{++}$  by means of guanidine carbonate*— $\text{NH} : \text{C}(\text{NH}_2)_2 \text{H}_2\text{CO}_3$ .<sup>11</sup> To the  $\text{H}_2\text{SO}_4$  solution, which must be dilute, add a dilute solution of ammonium tartrate (not quite neutral to methyl red). Then add an 8 per cent solution of guanidine carbonate. Boil. Ti is precipitated. Centrifuge or filter and wash the precipitate with ammonium tartrate solution and finally with ammonium nitrate. Dry and ignite;  $\text{TiO}_2$  is obtained. Confirm by other tests.

(d) *Separations by means of tannin*.<sup>12</sup> Fuse with  $\text{KHSO}_4$ . Dissolve in hot water; add a saturated solution of ammonium oxalate. Heat to boiling and add a hot solution of sodium salicylate and a hot solution of  $\text{CaCl}_2$ . Filter hot. Wash the precipitate at once with sodium salicylate solution until the washings are colorless. The precipitate contains most of the Cb and Ta. To the filtrate  $\text{NH}_4\text{Cl}$  is added, followed by a strong solution of tannin; Ti, Cb, and Ta are precipitated.

In oxalate-ammonium chloride solutions, made slightly alkaline with  $\text{NH}_4\text{OH}$ , tannin precipitates Zr, Th, Al, Fe, Cr,  $\text{UO}_2$ , but these elements are not precipitated in acid-oxalate- $\text{NH}_4\text{Cl}$  solutions.

(e) *Tungsten from Ti, Zr, Cb, Ta*.<sup>13</sup> Fuse the oxides with  $\text{K}_2\text{CO}_3$ . Treat the aqueous extract with a slightly ammoniacal solution of magnesium sulphate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 1 gram;  $\text{NH}_4\text{Cl}$ , 2 grams; water, 25 cc.;  $\text{NH}_4\text{OH}$ , 4 drops). Ti, Zr, Cb, Ta are precipitated; W remains in solution.

(f) *Separations by means of potassium sulphate*. Cold saturated solutions of  $\text{K}_2\text{SO}_4$  precipitate a potassium-zirconium sulphate insoluble in excess. Soluble in HCl, if the HCl solution is not heated; but, if heated, an insoluble basic salt is formed. Be, Al, Ti, U, Mo, W, V are not precipitated by a saturated  $\text{K}_2\text{SO}_4$  solution. Members of the cerium group of the rare earths are precipitated, but these sulphates are not soluble in cold dilute HCl (see page 309).

<sup>10</sup> See Lundell and Hoffman: *Outlines of Methods of Chemical Analysis*, p. 92.

<sup>11</sup> Jilek and Kota: *Coll. Czechos. Chem. Com.* 4, 412 (1932).

<sup>12</sup> Powell, Schoelter, and Co-workers: *Analyst* 54, 320 (1929); 55, 605 (1930); 57, 72, 550 (1932); 58, 143 (1933).

<sup>13</sup> Powell, Schoeller, and Jahn: *Analyst* 60, 506 (1935).

## DETECTION OF TIN

A. By Means of Cesium Chloride —  $\text{CsCl}$ ; or Rubidium Chloride —  $\text{RbCl}$ .

*Compounds Formed* —  $\text{Cs}_2\text{SnCl}_6$   
 $\text{Rb}_2\text{SnCl}_6$ .

The tin must be in solution in dilute  $\text{HCl}$  as stannic chloride, reacting as chlorostannic acid —  $\text{H}_2\text{SnCl}_6$ .

To the very dilute test drop an aqueous solution of either cesium chloride or rubidium chloride is added by Method I, page 31; or a fragment of the dry reagent may be added (Method II, page 33).

The crystals of cesium chlorostannate are always very small and require a high magnification for their resolution and identification (Fig. 45, page 69; Fig. 122, page 183). Ordinarily the crystals are discrete, colorless, highly refractive, isotropic octahedra, but thin square platelets and tiny cubes are sometimes formed. These crystals have been discussed under cesium and rubidium (*q.v.*, page 84).

Since rubidium chlorostannate is more soluble than the corresponding cesium salt, it separates in somewhat larger crystals, which are more easily found and their habit recognized; for this reason the rubidium salt is preferred by some analysts. The authors believe that the test with cesium is the more sensitive in experienced hands.

To render the tiny crystals somewhat more prominent, they can be colored yellow by having hydroiodic acid and a trace of free iodine present in the test drop. This is accomplished by introducing a very little  $\text{NaI}$  into the drop before the addition of the  $\text{CsCl}$  or  $\text{RbCl}$ ; the test drop should acquire a faint yellow color. An iodostannate is eventually formed and, entering into solid solution with the chlorostannate, colors the crystals of the latter a light yellow. It is essential to avoid an excess of  $\text{NaI}$  and also of  $\text{CsCl}$  or  $\text{RbCl}$ .

Cesium chloride forms a large number of readily crystallizable double chlorides (see page 152); for this reason it is always advisable first to separate the tin from other metals and compounds before testing with  $\text{CsCl}$ . If some of these double chlorides separate, they may interfere with, or mask, the tin reaction; or those which crystallize in isotropic octahedra may be mistaken for a tin reaction by an inexperienced analyst. Some anisotropic double chlorides separate in pseudo-octahedra; hence it is wise to examine preparations between crossed nicols. If barium and lead have not been removed, they sometimes cause trouble.

Water-soluble and acid-soluble materials may be treated with strong  $\text{HNO}_3$  (1 : 1) and evaporated to dryness at the temperature of boiling

water. This treatment is to be repeated several times in order to ensure the conversion of all the tin to an insoluble hydrous oxide (sometimes called "metastannic acid"). In its formation this hydrous oxide adsorbs all or part of any Sb, Bi, Cu, Pb, Fe, Zn which may be present. The insoluble tin compound is repeatedly extracted with dilute  $\text{HNO}_3$  to remove soluble substances and the residue dissolved in  $\text{HCl}$  (1 : 4) and tested for tin as outlined above.

Materials insoluble in water or in acids should be fused with alkali carbonate mixture or with  $\text{KHSO}_4$ , the fused mass evaporated with  $\text{HNO}_3$  as just described, and the hydrous oxide dissolved and tested as above.

If phosphates or arsenates are present, they are completely co-precipitated with the hydrous oxide of tin.

In the presence of much Cu, Au, Se, Te, the reaction for Sn may be seriously masked.<sup>14</sup>

If silver is present, and is not eliminated by the above treatment, tiny octahedra of  $\text{AgCl}$  will be formed.

An additional reason for always converting tin into metastannic acid and extracting all soluble material is to avoid error through the formation of "alums." If much  $\text{SO}_4^{--}$  is present and any alum-forming element, the addition of a cesium salt may be followed by the separation of octahedral crystals. The cesium alums are so very much more soluble than  $\text{Cs}_2\text{SnCl}_6$  that the octahedra of the alums grow much larger and are readily soluble in warm water, whereas cesium chlorostannate is always in very tiny crystals almost insoluble in warm water.

### Experiments.

- (a) Test dilute and concentrated solutions of tin.
- (b) Test for tin in an alloy.

### B. Recognition of Stannous Salts.

1. Identify tin by  $\text{CsCl}$  before proceeding to test for  $\text{Sn}^{++}$  (Test A, page 201).

2. Stannous salts give, with oxalic acid or alkali oxalates, stannous oxalate,  $\text{Sn}(\text{C}_2\text{O}_4)$ , separating in a great variety of prismatic or imperfectly developed crystals, mostly skeleton or dendritic forms, somewhat X-shaped but quite irregular. When elongated into prisms with a roof-like configuration the crystals exhibit parallel extinction but, as shown by Haushofer, characteristic twinning can be observed in which the extinction angle is  $14^\circ$  to  $15^\circ$  with the direction of elongation. These twins are usually thin plates with two parallel sides and irregular

<sup>14</sup> Short: *op. cit.*, p. 163.



re-entrant ends. It is probable that stannous oxalate is monoclinic (Fig. 88, page 119).

Stannic salts give no visible reaction with oxalic acid.

Stannous salts give a yellowish white precipitate with KI; and, if an excess of KI is added, a double salt is formed, separating in orange acicular crystals. Stannic salts yield at once a yellow precipitate.

3. Stannous salts, especially  $\text{SnCl}_2$ , reduce chloroauric acid with the formation of colloidal gold.

We can therefore identify  $\text{SnCl}_2$  by using  $\text{HAuCl}_4$  as a reagent and applying Cole's viscose-rayon test for gold.<sup>15</sup>

Evaporate to dryness the solution to be tested; dissolve in several large drops of water acidulated with HCl. Decant or filter. To the clear solution add an amount of pyrogallol about equal to the weight of  $\text{SnCl}_2$  probably present. Immerse in the drop a fiber of viscose-rayon about 5 mm. long. Warm gently and allow to evaporate to dryness. Dissolve the whole mass in water, warm, and evaporate again. Introduce the fiber into a tiny drop of moderately dilute  $\text{HAuCl}_4$ , following the suggestions given in Method VI, page 38.

If  $\text{SnCl}_2$  is present, that part of the fiber in the liquid will turn red, purple, or blue.

This test, though an excellent and exceedingly sensitive reaction for gold (see page 306), is not wholly dependable when applied in modified form for  $\text{Sn}^{++}$ , since it is difficult to prevent almost complete oxidation when only small amounts of tin are present.

## DETECTION OF LEAD

### A. By Means of Potassium Iodide — KI.

*Compound Formed* —  $\text{PbI}_2$ .

The reagent is applied by Method I, page 31, to the not too dilute test drop faintly acidified with  $\text{HNO}_3$ .

Lead iodide —  $\text{PbI}_2$  — separates at once in bright yellow, thin scales and hexagonal plates (Fig. 138, page 205), that appear to be greenish, brownish, or even gray by transmitted light. By reflected light the plates and scales scintillate and glisten with iridescent colors as they turn over in the solution (colors of thin films) — a characteristic that is peculiar to yellow hexagonal plates of  $\text{PbI}_2$ . Lead iodide is soluble in a *large excess* of KI, the double salt  $\text{PbI}_2 \cdot \text{KI} \cdot 2 \text{H}_2\text{O}$  being formed. Too much  $\text{HNO}_3$  will cause a decomposition of the  $\text{PbI}_2$  with the formation of  $\text{Pb}(\text{NO}_3)_2$ , and this being a salt of low solubility it will separate in the form of isotropic, highly refractive, colorless octahedra. The

<sup>15</sup> Cole, H. I.: *Philippine Jour. Sci.* 21, 361 (1922).

appearance of clear, colorless, octahedral crystals under these conditions should be considered indicative of the presence of lead. Strontium, barium and arsenic give isotropic, regular octahedra separating in a test drop acidulated with  $\text{HNO}_3$ , but only if much concentrated  $\text{HNO}_3$  is present.

$\text{PbI}_2$  is moderately soluble in hot water, from which on cooling it again separates in large, beautifully formed hexagons. To obtain the best results a large drop of water faintly acidified with  $\text{HNO}_3$  is essential. In the absence of  $\text{HNO}_3$  a basic salt may result.

Lead forms double iodides with many elements.<sup>16</sup> Most of these double salts crystallize well, but their solubilities are sufficiently great to keep them in solution until the test drop passes almost to dryness.

From neutral or slightly alkaline solutions, especially those of lead salts of organic acids, basic iodides are apt to form, such as  $\text{PbI}_2 \cdot \text{PbO}$ ,  $\text{PbI}_2 \cdot 2 \text{PbO}$ , and others, all of uncertain composition. These basic salts may interfere with or obscure the formation of the normal salt.

Heated with  $\text{HCl}$ , the  $\text{PbI}_2$  is dissolved, and, upon cooling, crystals of the normal iodide  $\text{PbI}_2$ , normal chloride  $\text{PbCl}_2$ , and chloriodides  $\text{PbCl}_2 \cdot \text{PbI}_2$  and  $2 \text{PbCl}_2 \cdot \text{PbI}_2$  separate. The chloriodides appear as acicular crystals having a faint yellow color. Usually the normal iodide is destroyed.

Salts of copper, antimony, and bismuth, if present in moderate amounts, seriously interfere with the  $\text{KI}$  test for lead, since they readily unite with  $\text{KI}$  to form insoluble iodides, and in the presence of lead complex compounds are formed that separate as dark, reddish-brown, sandy precipitates. Boiling the diluted test drop, slightly acidified with  $\text{HNO}_3$ , will usually cause a decomposition of these complex salts, and on cooling typical crystals of  $\text{PbI}_2$  can be obtained. Even a very little bismuth may (if the conditions are right) lead to the formation of orange-red disks and irregular plates having no resemblance to  $\text{PbI}_2$ .

In the event of evidence being obtained of the possible presence of antimony or bismuth, proceed as follows: to a very dilute solution add a very little dilute  $\text{H}_2\text{SO}_4$ ; filter, or centrifuge, and test the precipitate with  $\text{KI}$ .

For a discussion of the other elements that are precipitated by  $\text{KI}$ , see Mercury, page 158.

If lead, only, is to be tested for, it is generally better to add the  $\text{KI}$  by Method II, page 33.

According to Groth,<sup>17</sup>  $\text{PbI}_2$  is to be referred to the hexagonal system.

<sup>16</sup> Mosnier: *Ann. Chim. Phys.* (7) 12, 374 (1897).

<sup>17</sup> *Elemente d. Phys. u. Chem. Krystallographie* (Oldenbourg, München, 1921), pp. 275, 306.

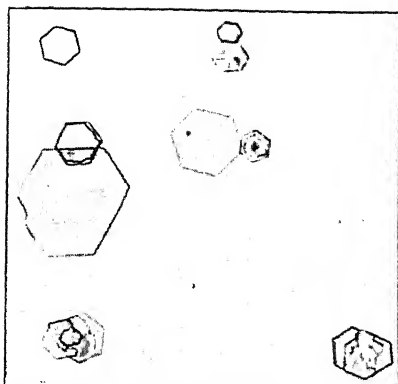


FIG. 138. Lead with Potassium Iodide. 100 $\times$ .

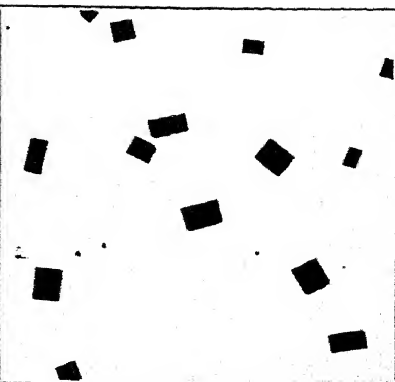


FIG. 139. Lead with Potassium Nitrite and Copper Acetate. 100 $\times$ .

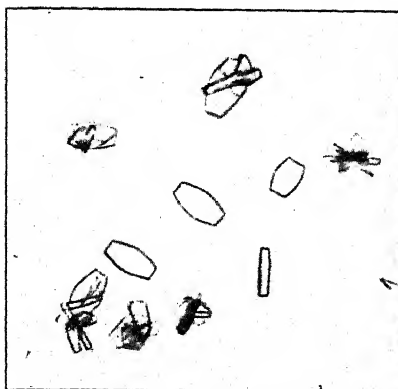


FIG. 140. Vanadium Precipitated as Ammonium Metavanadate. 400 $\times$ .

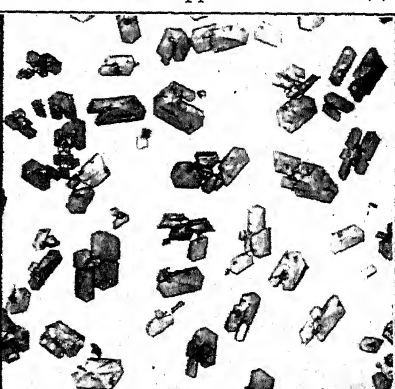


FIG. 141. Ammonium Metavanadate Recrystallized from Acetic Acid. 100 $\times$ .

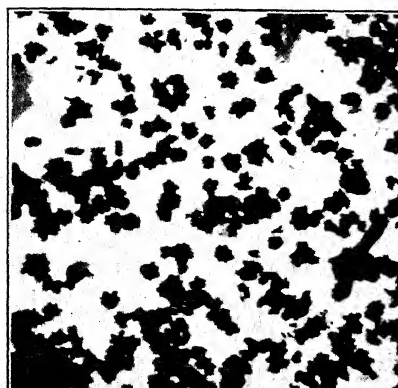


FIG. 142. Vanadium Precipitated as Silver Pyrovanadate. 400 $\times$ .

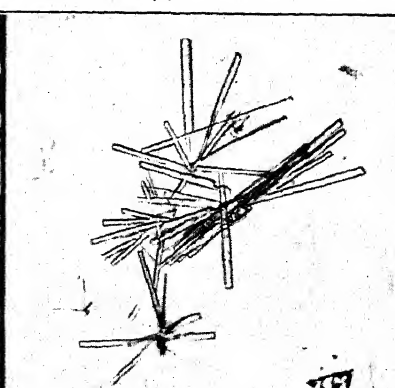


FIG. 143. Tantalum with Potassium Fluoride. 100 $\times$ .

$\text{PbCl}_2$  and  $\text{PbBr}_2$  are orthorhombic and form isomorphous mixtures with each other but not with  $\text{PbI}_2$ .

#### Experiments.

(a) To a test drop containing  $\text{Pb}(\text{NO}_3)_2$  add KI. Study the preparation, then add a drop of water and heat to boiling. After the drop has cooled, study it again. Repeat the experiment, but this time use an excess of KI. Try again in acidified solution.

(b) Make a preparation of  $\text{PbSO}_4$ . Decant the mother liquor, add to the sulphate residue a drop of water, acidify with  $\text{HNO}_3$ , then add a fragment of KI. After a few seconds examine the preparation.

(c) Make a mixture of Pb and Ag; test with KI. Then try in turn mixtures of Pb and Sb; Pb and Bi; Sb and Bi; Pb and Cu; Pb and Sn; Pb and Hg.

### B. By Means of Hydrochloric Acid — $\text{HCl}$ .

#### *Compound Formed* — $\text{PbCl}_2$ .

The method of applying the reagent and the general properties of the reaction product have been discussed under Mercury, Method B, page 156.

Since  $\text{PbCl}_2$  is only slightly soluble in cold water but quite soluble in hot water, the test drop should be cold before the reagent is added; it is also essential that the test drop shall be moderately concentrated and slightly acidified with  $\text{HNO}_3$ . In strictly neutral solutions of lead acetate containing elements of Group I, the addition of  $\text{HCl}$  (if not in excess) may cause the precipitation of colorless, highly refractive ( $n = 2.08 +$ ) orthorhombic prisms believed to have the formula  $\text{Pb}(\text{OH})\text{Cl}$ ; but sometimes monoclinic prisms are formed.

Too much  $\text{HNO}_3$  may lead to the separation of glittering isotropic octahedra of  $\text{Pb}(\text{NO}_3)_2$ , for this salt is of low solubility and almost insoluble in  $\text{HNO}_3$ .

$\text{PbCl}_2$  is more soluble in water acidified with  $\text{HNO}_3$  than in pure water; hence the precipitation of the lead is never complete. It is differentiated from the chlorides of  $\text{Ag}^+$  and  $\text{Hg}^+$  by its solubility in hot water. On cooling there are obtained pseudohexagonal plates, prisms, and rhombs. The thin six-sided prisms are especially characteristic and can be seen to be the fully developed crystals, of which the X-shaped crystals, in the cold, are skeletons (Figs. 124, 125, page 183).

$\text{PbCl}_2$  forms with chlorides of the elements of Group I a large number of readily soluble, double chlorides, all of them with habits very different from that of the normal chloride. It is quite important that the analyst shall be familiar with at least the double cesium salt — cesium chloroplumbate — since crystals of this compound are not infrequently obtained when  $\text{CsCl}$  is used in testing for cadmium, tin, antimony, and bismuth. Cesium chloroplumbate  $4\text{CsCl} \cdot \text{PbCl}_2$  usually separates in

rhombohedral tablets, but when they are small and thin they appear to be square and rectangular plates with parallel extinction.

For the appearance and characteristics of  $\text{HgCl}$ ,  $\text{AgCl}$ ,  $\text{TlCl}$ , see page 155.

A fragment of  $\text{KI}$  added to a test drop containing  $\text{PbSO}_4$  or  $\text{PbCl}_2$  gives a precipitate of  $\text{PbI}_2$ .

#### Experiments.

(a) To a drop of a concentrated solution of  $\text{Pb}(\text{NO}_3)_2$  add a drop of dilute  $\text{HCl}$  in the manner described above. Make several other preparations, varying the concentrations of the test drops.

(b) Recrystallize a preparation of  $\text{PbCl}_2$  by heating to boiling with a large drop of water.

(c) Precipitate  $\text{PbCl}_2$  in the presence of an alkali chloride.

#### C. By Means of the Triple Nitrite Reaction.

*Compound Formed* —  $2 \text{KNO}_2 \cdot \text{Cu}(\text{NO}_2)_2 \cdot \text{Pb}(\text{NO}_2)_2$ .<sup>18</sup>

Since it is essential that the test drop be as concentrated as possible, it is simplest to adopt the procedure of Schoorl<sup>19</sup> and evaporate the solution to dryness. The dry residue is covered with a small drop of moderately concentrated acetic acid, a fragment of  $\text{Na}(\text{C}_2\text{H}_3\text{O}_2)$  is added, and when all is dissolved a large fragment of  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$  is added and allowed to dissolve. Finally a fragment of  $\text{KNO}_2$  is introduced at the center of the drop and the preparation is allowed to stand for a few seconds.

If lead is present, there will be formed a triple nitrite of potassium, copper, and lead. This salt separates in tiny isotropic square and rectangular plates, and in cubes and rectangular prisms which unless very thin are jet black by transmitted light but appear brownish by reflected light (Fig. 139, page 205). Thin plates and prisms may be brown or orange colored by transmitted light. On standing, these crystals thicken and become black.

Although the reaction requires a slight excess of  $\text{KNO}_2$ , too great an excess should be carefully avoided, since the triple nitrite is soluble in an excess of alkali nitrite.

The best results are obtained when copper is in slight excess of the lead present in the material being tested.<sup>20</sup>

In the absence of  $\text{Ca}$ ,  $\text{Sr}$ , and  $\text{Ba}$  this test is specific for lead.

In the salt  $2 \text{KNO}_2 \cdot \text{Cu}(\text{NO}_2)_2 \cdot \text{Pb}(\text{NO}_2)_2$ , potassium may be replaced

<sup>18</sup> This salt is a member of the isomorphous series —  $(\text{K}, \text{Rb}, \text{Cs}, \text{Tl})_2 (\text{Pb}, \text{Ca}, \text{Sr}, \text{Ba}) (\text{Cu}, \text{Co}, \text{Ni}) (\text{NO}_2)_6$ .

<sup>19</sup> *Beiträge z. mikrochem. Anal.* (Wiesbaden, 1909), p. 22.

<sup>20</sup> Mayrhofer: *Mikrochem. d. Arzneimittel u. Gifte*, p. 134, has shown that to obtain the best results the ratio of copper to lead should be about 10 : 1.

by rubidium, cesium, or thallium, the solubility decreasing in the order named. The sensitivity of this reaction for lead may be apparently increased by introducing into the test drop cesium or thallium. Nickel and mercury can replace copper, and calcium, strontium, and barium can replace lead.

With nickel the salt formed is believed to have the formula  $2 \text{KNO}_2 \cdot \text{Ni}(\text{NO}_2)_2 \cdot \text{Pb}(\text{NO}_2)_2$ . This salt also crystallizes in square and rectangular plates and in cubes and rectangular prisms; *i.e.*, with a habit similar to that of the copper salt, but the crystals are much smaller and are yellowish-brown in color, never black.

Cobalt forms with members of the potassium group, and with  $\text{NH}_4^+$ , a very difficultly soluble double nitrite,  $3 \text{R NO}_2 \cdot \text{Co}(\text{NO}_2)_3 \cdot 1\frac{1}{2} \text{H}_2\text{O}$ , which immediately separates as an exceedingly fine, granular, faintly reddish-brown precipitate, or, more rarely, as very tiny cubes and regular octahedra. The corresponding nickel double nitrite is much more soluble and appears as tiny, yellow, four-sided plates and tables, or as yellow cubes and rectangular tablets, but these crystals are never black. In the presence of cobalt the test for lead or copper will usually fail because of the formation of the difficultly soluble potassium cobaltinitrite. It is then essential to decant after the cobalt has been precipitated, concentrate the decanted solution, and add more nitrite; but even under these conditions the results are not satisfactory.

Rhodium is precipitated as  $3 \text{KNO}_2 \cdot \text{Rh}(\text{NO}_2)_3$  in spheres and yellow cubes which cannot readily be distinguished from those formed by cobalt (Fig. 172, page 275). Palladium forms long, thin, curving lemon-yellow prisms as the test drop passes to dryness. The other members of the platinum group do not interfere with the precipitation of cobalt.

The triple nitrite reaction can be used to advantage in testing for copper by omitting the copper acetate and proceeding otherwise as directed. This reaction is especially useful in testing material thought to contain both lead and copper, as it is capable of yielding results more rapidly than other available methods. In such cases the dry material is covered with acetic acid, sodium acetate is added, then the  $\text{KNO}_2$ . If no black cubes appear, add a little  $\text{CsCl}$  in order to increase the sensitivity of the reaction. The appearance of black cubes points to the presence of both lead (or barium) and copper. In the presence of copper the reaction for nickel is masked by the deep black copper salt.

Unlike most micro reactions the test drop may be allowed to pass to dryness, before the final observations are made. The jet-black crystals are usually readily discovered amidst the confused mass of other crystalline substances.

The substitution of  $\text{NaNO}_2$  for  $\text{KNO}_2$  and the introduction of

$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  as well as  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$  into the test drop convert the triple nitrite reaction into an excellent test for  $\text{K}^+$  (or members of the potassium group). The size of the black cubes affords a possible though very uncertain means of distinguishing between  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ , and  $\text{Tl}^+$  since the potassium triple salt grows largest and the  $\text{Tl}^+$  smallest.

The triple nitrite reaction may be brought about in a variety of ways in the testing of material of unknown composition. The following outline may serve as an indication of some of its manifold uses. In all the examples cited, it is assumed that the solution to be tested has been evaporated to dryness, that a drop of acetic acid and a fragment of sodium acetate have been added to the dry residue before the application of the nitrite.

*I. Add a fragment of pure  $\text{NaNO}_2$ .<sup>21</sup>*

- (a) An exceedingly fine reddish-brown precipitate is formed:  
Co and either K, Rb, Cs, Tl, or  $\text{NH}_4$ .
- (b) Black plates and cubes:  
Cu and Pb plus K, Rb, Cs, Tl,  $\text{NH}_4$ ; or Cu and Ca, Sr, Ba plus K, Rb, Cs, Tl,  $\text{NH}_4$ .
- (c) White granular precipitate:  
Pb and Hg plus K, Rb, Cs, Tl,  $\text{NH}_4$ .

*II. No precipitate was obtained in I. Add  $\text{KNO}_2$ .*

- (d) A fine reddish or yellowish precipitate is formed:  
Co or Rh.
- (e) Yellow plates and cubes:  
Ni and Pb (Co, Rh), Ca, Sr, Ba.
- (f) Black plates and cubes:  
Pb and Cu, or Sr and Cu, or Ba and Cu, or mixtures (Ni, Co).
- (g) White granular precipitate:  
Pb and Hg, or Sr and Hg, or Ba and Hg or mixtures.

*III. No test was obtained in II. Add  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ .*

- (h) Black plates and cubes:  
Pb (Sr, Ba).

*IV. No test was obtained in III. Prepare a fresh film of the original material, add a fragment of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , then add  $\text{HC}_2\text{H}_3\text{O}_2$ ,  $\text{NaC}_2\text{H}_3\text{O}_2$ , and finally  $\text{KNO}_2$ .*

- (i) Black plates and cubes:  
Cu (Ni).
- (j) Yellow plates and cubes:  
Ni, Co, or Rh, or mixtures.

<sup>21</sup> The  $\text{NaNO}_2$  must be free from potassium. Since most  $\text{NaNO}_2$  of commerce contains potassium, it is always necessary to make a "blank" test with cobalt acetate in order to be sure of the purity of the reagents. For a method for the purification of sodium nitrite, see Noyes and Bray: *Qualitative Analysis for the Rare Elements* (Macmillan, New York, 1927), p. 486.

*Note.* The addition of  $\text{NaNO}_2$  or  $\text{KNO}_2$  may lead to the separation of  $\text{AgNO}_2$  in long, slender, greenish-yellow needles or prisms.

The addition of  $\text{NaC}_2\text{H}_3\text{O}_2$  or  $\text{HC}_2\text{H}_3\text{O}_2$  may cause a separation of  $\text{Ag}(\text{C}_2\text{H}_3\text{O}_2)$ .

Under exceptional conditions  $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)$  may be formed.

Much antimony, bismuth, cadmium, or mercury may, under certain conditions, interfere with the test for lead.

(See also Rare Earths, page 312.)

#### Experiments.

- (a) Test a preparation containing Pb by the triple nitrite reaction.
- (b) Try another preparation, this time introducing Cs.
- (c) By a series of careful dilutions determine the limit of the precipitation of Pb as the K salt, the Cs salt, and the Tl salt.
- (d) Test a mixture of Pb and Ni; Pb and Co; Pb and Ag.

#### D. By Means of Sulphuric Acid — $\text{H}_2\text{SO}_4$ .

*Compound Formed* —  $\text{PbSO}_4$ .

The formation and the properties of  $\text{PbSO}_4$  have been discussed under the  $\text{H}_2\text{SO}_4$  reactions of the Alkaline Earths. (See page 106.)

$\text{PbSO}_4$  separates as a fine granular precipitate. Decant, wash, and test as below.

Boil with  $\text{HNO}_3$ ; rectangular plates and rhombs separate on cooling. In rare cases octahedra of  $\text{Pb}(\text{NO}_3)_2$  may be obtained.

Heat with concentrated  $\text{H}_2\text{SO}_4$  until white fumes are evolved. Cool and breathe upon the drop. Spindle-shaped crystals and irregular skeleton or dendritic crystals or aggregates are obtained (Fig. 123, page 183).

Treat with KI.  $\text{PbI}_2$  is formed.

$\text{PbSO}_4$  is soluble in  $(\text{NH}_4)\text{C}_2\text{H}_3\text{O}_2$ .

#### Other Reactions of Lead.

- (a) With oxalic acid, see page 114 (Alkaline Earths).
- (b) With potassium or ammonium bichromate; see page 280 (Silver).
- (c) With sodium bicarbonate; see page 145 (Zinc).
- (d) With alkali tartrates; see page 72 (Potassium).
- (e) With potassium antimonyl tartrate; see page 238 (Antimony).
- (f) With nitric acid.  $\text{Pb}(\text{NO}_3)_2$  is difficultly soluble in  $\text{HNO}_3$  and may therefore separate when this acid is used as a solvent.  $\text{Pb}(\text{NO}_3)_2$  forms colorless, highly refractive isotropic octahedra.

**General Method for "Opening Up" the Material, in Testing for the Elements of Groups IV and V.** — The finely powdered material is fused in a platinum cup with about five times its volume of sodium



pyrosulphate.<sup>22</sup> The fusion should be carried out at a temperature below the driving off of  $\text{SO}_3$ .

Dissolve in hot water, acidifying with  $\text{H}_2\text{SO}_4$ . The insoluble residue may contain Si, Ge, Cb, Ta, Ba, Sr, Ca, Pb, Ti, Zr, Fe, Sn, and W.

For methods for the removal of Ba, Sr, Ca, and Pb, see the Alkaline Earths, page 128.

Fuse the residue with  $\text{NaOH}$ , dissolve in cold water; filter. Sodium silicate is soluble, but sodium columbate and sodium tantalate are relatively insoluble in  $\text{NaOH}$ .

To the  $\text{NaOH}$  solution add  $\text{HCl}$  to precipitate the silica; filter; wash; dissolve part of the  $\text{SiO}_2$  in  $\text{HF}$  or  $\text{NH}_4\text{F} \cdot \text{HF} + \text{HCl}$  on a celluloid or cellulose acetate slide, and add  $\text{NaCl}$ .

To another part of the precipitated "silica" add  $\text{HF}$  and heat to drive off  $\text{SiF}_4$ . Repeat the treatment several times until the residue no longer diminishes in amount. Test the residue for Ti and Zr.

The above separation method is in no case quantitative, and the results obtained must be interpreted with great care.

<sup>22</sup> Putnam, Roberts, and Selchow: *Amer. Jour. Sci.* 15, 101 (1928). The reagent is prepared by heating pure  $\text{HNaSO}_4$  in a platinum crucible, until all water has been expelled and fumes of  $\text{SO}_3$  begin to rise. Cool, pulverize, and keep in a sealed bottle.

## CHAPTER VII

### DETECTION OF THE ELEMENTS OF GROUP V

N; V, Nb, Ta; P, As, Sb, Bi

In Group V the transitional element nitrogen affords practically no micro reactions that correlate it with the other members of the group.

The subgroup containing vanadium, columbium, and tantalum is closely related to silicon, titanium, zirconium, germanium, and tin; like these elements vanadium, columbium, and tantalum are acidic, and salts in which they function as cations are rarely, if ever, encountered in routine qualitative analyses. Save in the case of some of the newer alloys, the only compounds normally met with are vanadates, columbates, and tantalates. But the resemblances are not alone with Group IV, for we find in certain reactions of analytical importance that a close analogy exists with chromium, molybdenum, and tungsten of Group VI; the analogies are especially true as regards the element vanadium, but to a less degree for columbium and tantalum. There is also a somewhat closer relationship between the two subgroups of Group V than is shown by the subgroups of the other vertical groups of the Periodic System. This is shown by the isomorphism of the orthovanadates with the orthophosphates and orthoarsenates. So too we have metavanadates and metaphosphates behaving similarly. Moreover, as we have alkali silicomolybdates and tungstates, so we find alkali vanado-, phospho-, and arseno-molybdates and tungstates, all soluble in water.

Columbium and tantalum resemble titanium and zirconium more closely in their analytical behavior than they do the other elements of Groups IV and V. These two elements are so closely related that in most cases their microscopical differentiation is impracticable, particularly when only small amounts of material are available; for their micro reactions are based mainly upon the relative solubilities of reaction products rather than upon crystal habit, hence positive identification is exceptionally difficult.

Most of the salts containing phosphorus with which we have to deal are isomorphous with those containing arsenic; nevertheless, the micro-differentiation of these two elements is not at all difficult. Like the elements of the first subgroup, phosphorus and arsenic function chiefly

as anions. The transition from these acidic elements to the basic elements antimony and bismuth is very marked; nevertheless antimony and arsenic have much in common, and the logical grouping is that of the triad, phorus-arsenic-antimony, with bismuth standing quite apart. In spite of this apparently well-marked division, one of the difficult problems of microscopical qualitative analysis is proving, beyond doubt, the presence of both antimony and bismuth in complex mixtures.

### DETECTION OF VANADIUM

In order successfully to separate and identify vanadium, it is essential that its important chemical properties shall be kept in mind.

Vanadium forms four oxides,  $\text{VO}$ ,  $\text{V}_2\text{O}_3$ ,  $\text{VO}_2$  and  $\text{V}_2\text{O}_5$ , giving rise to lavender or violet, green, blue, and yellow compounds, respectively.

From  $\text{V}_2\text{O}_3$  there is formed  $\text{V}_2(\text{SO}_4)_3$ , which is able to unite with alkali sulphates to form vanadium alums. In this respect  $\text{V}^{+++}$  resembles  $\text{Cr}^{+++}$  and  $\text{Fe}^{+++}$ ;  $\text{VSO}_4 \cdot 7\text{H}_2\text{O}$  is known, an analogy with  $\text{Fe}^{++}$ .

$\text{V}_2\text{O}_3$  is readily oxidized to  $\text{V}_2\text{O}_5$ , the analogue of  $\text{P}_2\text{O}_5$ , whence we have orthovanadates (from  $\text{H}_3\text{VO}_4$ ) and metavanadates (from  $\text{HVO}_3$ ). The latter are easily converted into the former when heated in acidified solution.

Unlike phosphorus and arsenic, the trichloride cannot be separated by distilling in a current of chlorine, for  $\text{VCl}_3$  is non-volatile and crystallizes in deliquescent plates. But  $\text{VCl}_4$  and  $\text{VCl}_5$  are distillable, high-boiling liquids.

$\text{H}_2\text{O}_2$  oxidizes solutions of vanadates to pervanadates, *e.g.*,  $\text{KVO}_4$ , a salt analogous to  $\text{KMnO}_4$ .

By precipitations we usually obtain the metavanadate, but in fusions with oxidizing agents ortho- (or pyro-) vanadates are formed.

#### A. Precipitation by Ammonium Chloride — $\text{NH}_4\text{Cl}$ .

*Compound Precipitated* —  $\text{NH}_4\text{VO}_3$ .

To a drop or two of an alkaline solution, believed to contain vanadium, add by Method I a completely saturated solution of  $\text{NH}_4\text{Cl}$ , or add large crystals of  $\text{NH}_4\text{Cl}$ .

Ammonium metavanadate is precipitated in the form of colorless elliptical plates or tiny lenticular, strongly birefringent orthorhombic grains (Fig. 140, page 205). Since this is essentially a method of "salting out," it is important that the test drop shall be concentrated with respect to vanadium. It follows that many other salts may be precipitated with the  $\text{NH}_4\text{VO}_3$  and may completely mask the reaction.

These colorless crystals  $\text{NH}_4\text{VO}_3$  can be converted into a yellow

ammonium vanadate of uncertain composition by adding dilute acetic acid and heating the solution. This is accomplished by decanting the supernatant liquid, adding two or three drops of acetic acid, and heating until the metavanadate has dissolved and part of the water evaporated. On standing, as the preparation passes to dryness, yellow four-sided and six-sided plates and tabular crystals separate (Fig. 141, page 205). The four-sided plates have an acute angle of  $68^\circ$  and the six-sided are fourlings with extinction angles of  $29^\circ$  with their elongation; star-like radiating clusters and skeleton forms also separate.

### B. By Means of Silver Nitrate — $\text{AgNO}_3$ .

#### *Compound Formed* — $\text{Ag}_4\text{V}_2\text{O}_7$ .<sup>1</sup>

To a moderately concentrated solution of material precipitated by  $\text{NH}_4\text{Cl}$  and thought to be  $\text{NH}_4\text{VO}_3$ , add a large drop of moderately concentrated acetic acid; warm gently. If the drop contains vanadium, the solution should turn yellow. Place at the edge of the test drop a large fragment of  $\text{AgNO}_3$ . Heat the preparation so that both reagent and test drop are hot. While still holding the preparation over the micro flame, cause the dissolved  $\text{AgNO}_3$  to flow into the test drop. Allow the preparation to stand for some time. If vanadium is present, a dense orange-red precipitate is obtained; and, if the conditions are favorable, crystallization takes place, and tiny bristling disks or slender needles or slender prisms, singly, in clumps, and in radiating clusters, are formed (Fig. 142, page 205). These crystals are yellow, orange, dark-red, or brown, or may even be black in appearance. In order to separate the silver vanadate from silver chloride, the silver vanadate formed is dissolved in  $\text{HNO}_3$ , filtered, and the filtrate is reprecipitated by  $\text{NaC}_2\text{H}_3\text{O}_2$ .

The character of the first precipitate varies with concentrations and the degree of the acidity with  $\text{HC}_2\text{H}_3\text{O}_2$ . It may be a dense, curdy, yellow precipitate or yellow acicular crystals or thin irregular plates.  $\text{Ag}_3\text{AsO}_4$  behaves in a similar way. (See Silver, page 282.)  $\text{Ag}_3\text{PO}_4$  forms a yellowish, white, curdy precipitate changing into three-armed skeleton crystals. Crystals of silver acetate may obscure the test.

It is often advantageous first to allow the acetic acid solution of  $\text{V}_2\text{O}_5$  to pass to dryness. Very soluble yellow plates are formed exhibiting oblique extinction and weak dichroism; thick plates may be orange or even reddish in color. Having noted the presence of these crystals, add a drop of acetic acid and proceed with the completion of the test.

<sup>1</sup> Behrens: *Anleitung*, p. 73.

### Separations.

1. Fuse the material with  $\text{KNO}_3$ , forming potassium vanadate, which is soluble in water. Add  $\text{Pb}(\text{NO}_3)_2$  or  $\text{BaCl}_2$ , precipitating the V as Pb or Ba vanadate. Decompose the vanadate with  $\text{H}_2\text{SO}_4$  and neutralize the vanadic acid with  $\text{NH}_4\text{OH}$ . Add a saturated solution of  $\text{NH}_4\text{Cl}$ , thus precipitating  $\text{NH}_4\text{VO}_3$ .

2. Decompose the material with concentrated  $\text{HNO}_3$ . Evaporate the solution. Treat the residue with a concentrated solution of  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ . Sodium vanadate is soluble. Add  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$ , precipitating the meta-vanadate. If Pb is present, it should be removed by  $\text{H}_2\text{S}$  before the treatment with  $\text{NaOH}$ .

3. Vanadium from Tungsten in Steel.<sup>2</sup> Dissolve 2 grams in 50 cc. of 5 per cent  $\text{H}_2\text{SO}_4$ ; boil. The insoluble residue contains V and W. Wash with hot water. Digest with 40 cc. of concentrated  $\text{HCl}$ . Heat to boiling and add dropwise 25 drops of concentrated  $\text{HNO}_3$ . Evaporate to small bulk, add several drops of water, and centrifuge. Vanadium will be in the solution; tungsten as insoluble  $\text{WO}_3$ .

### Miscellaneous Reactions.

$\text{K}_4\text{Fe}(\text{CN})_6$ : gives a heavy green precipitate insoluble in acids.

Oxalic Acid: reduces to tetravalent V, blue color.

$\text{H}_2\text{O}_2$ : reddish-brown solution, yellow (or orange), with Ti, Ce, Cb, (Ta).

Metallic Zn, in  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ , reduces to tetravalent V; solution is first green, then blue, then green, and finally lavender blue (divalent V) or violet. Columbates give blue—Tantalates no color. Titanates, blue. Molybdates, blue. (Ru and Rh blue.)

With strychnine sulphate in concentrated  $\text{H}_2\text{SO}_4$ , bluish-violet coloration changing to rose pink. No color with Cb, Ta, Ti, W.

### DETECTION OF COLUMBIUM AND TANTALUM

Unless a considerable quantity of material, relatively high in either columbium or tantalum, is available, the positive identification of these elements is impracticable by micro methods. Recourse should be had to the spectrograph, or the analyst should be contented to group the two elements together and report columbium and tantalum present or absent, since none of the procedures outlined below are wholly satisfactory on a microscopical scale.

Differentiation when dealing with relatively pure materials is always possible, but identification of each element when both are present in complicated mixtures is impracticable.

<sup>2</sup> Färber: *Chem. Ztg.* 55, 691 (1931).

In microanalysis columbates or tantalates derived from  $\text{Cb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$  are alone encountered. Usually a preliminary test with metallic zinc or metallic tin in  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  solution is advisable. Columbates give a blue to brown color resulting from reduction to  $\text{CbO}_2$  and  $\text{CbO}$  (and even to  $\text{Cb}$  in part). Tantalates give no color. The blue color is, however, not peculiar to columbium, as we have already seen. (See  $\text{Ti}$ ,  $\text{V}$ ,  $\text{Mo}$ ,  $\text{W}$ .)

Because of the possible interference of many substances, it is necessary first to accomplish a separation before applying identity tests.

### Outline of Procedures for the Separation of Columbium and Tantalum<sup>3</sup>

(a) The material is fused with several times its volume  $\text{HNaSO}_4$  at a bright red heat. The melt is extracted with water, filtered, and the residue is thoroughly washed with hot  $3\text{ N HCl}$  to remove the iron, manganese, and other soluble substances.  $\text{HCl}$  of this concentration dissolves no columbium or tantalum, but more dilute  $\text{HCl}$  will cause a loss. The white residue containing columbium and tantalum is then treated with  $\text{H}_2\text{SO}_4$  (1 : 1) and heated until boiling ceases. The precipitate is separated by the centrifuge and the residue washed with cold  $6\text{ N H}_2\text{SO}_4$  until the washing liquid gives no precipitate with  $\text{NH}_4\text{OH}$ . Columbium is completely dissolved and tantalum remains in the residue. This procedure is especially applicable to columbite and tantalite.

(b) Precipitation by Phosphates, page 199.

(c) Precipitation by Tannin, page 200.

(d) Fuse the material with sodium pyrosulphate (see page 210). Dissolve in boiling water acidified with  $\text{H}_2\text{SO}_4$ . Centrifuge and wash the insoluble residue. Dry, fuse with  $\text{NaOH}$ . Dissolve in cold water; sodium silicate is soluble but sodium columbate and sodium tantalate are insoluble providing that an excess of  $\text{NaOH}$  is present. Centrifuge and wash the precipitate with  $\text{NaOH}$  solution to remove sodium silicate. Pour off the supernatant solution and carefully add dilute  $\text{HCl}$ . The precipitate of hydrous oxides which is first formed should be wholly ( $\text{Cb}$ ) or partly ( $\text{Ta}$ ) soluble in an excess of the acid. This solution may be used for identification tests.

(e) The hydrous pentoxide of columbium is substantially insoluble if boiled with concentrated  $\text{HCl}$ , but if the concentrated acid is decanted and water added to the moist residue the latter passes into "solution."

<sup>3</sup> Sears: *Jour. Amer. Chem. Soc.* 48, 343 (1926).

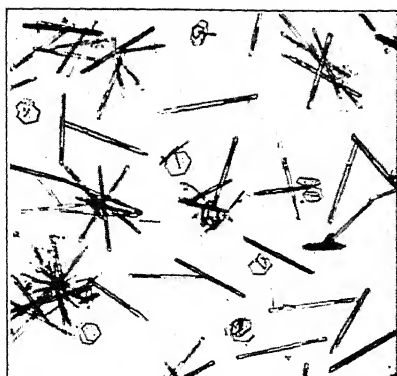


FIG. 144. Columbium Precipitated as Sodium Columbate. 200 $\times$ .

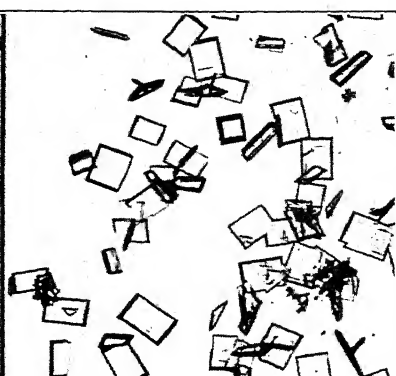


FIG. 145. Sodium Columbate Recrystallized from Hot Water. 100 $\times$ .

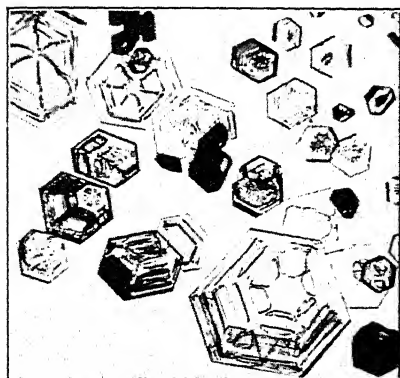


FIG. 146. Antimony with Cesium Chloride. 100 $\times$ .

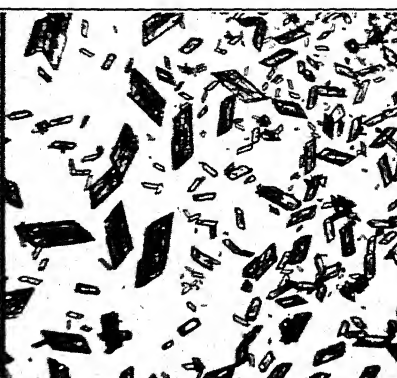


FIG. 147. Antimony with Cesium Chloride in the Presence of too much Nitric Acid. 100 $\times$ .

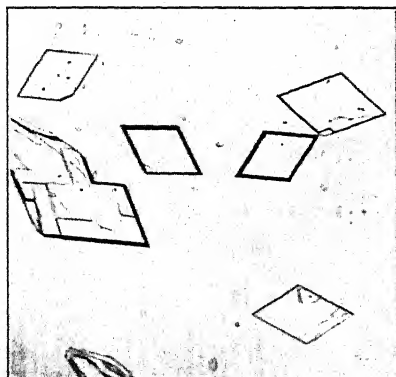


FIG. 148. Bismuth with Cesium Chloride in Excess. 100 $\times$ .

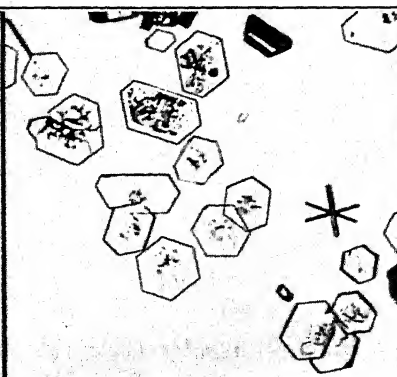


FIG. 149. Bismuth with Cesium Chloride not in Excess. 150 $\times$ .

This sol may be used for tests. The hydrous pentoxide of tantalum is not completely peptized under these conditions.

(f) To freshly precipitated columbium hydrous pentoxide add dilute HCl and an equal volume of  $\text{H}_2\text{O}_2$ ; boil. A clear solution can be obtained, but in the case of tantalum the solution is incomplete.

(g) Dissolve the oxides in a mixture of HF and  $\text{HNO}_3$ . Evaporate to dryness. Cool and dissolve the residue in HF. Test drops upon a non-silicic object slide by carefully adding  $\text{K}_2\text{CO}_3$ . Potassium fluotantalate separates almost at once, but potassium fluocolumbate yields a crystalline precipitate only on standing for some time. See Method X, page 43, for precautions which must be observed when dealing with fluorides; also pages 62, 180, 190.

(h) To the cold, dilute aqueous solution of a fusion with NaOH add dilute  $\text{H}_2\text{SO}_4$ ; the hydrous pentoxides of Cb and Ta are precipitated. Centrifuge, pour off the clear solution. To the residue add a little concentrated  $\text{H}_2\text{SO}_4$  and heat to dissolve the oxides. Cool and add water; Cb is dissolved; Ta is reprecipitated.

#### A. By Means of Hydrofluoric Acid — HF — and Potassium Fluoride — KF.

*Compounds Formed* —  $\text{K}_2\text{CbF}_7$  or  $2 \text{KF} \cdot \text{CbO} \cdot \text{F}_5 \cdot \text{H}_2\text{O}$   
 $\text{K}_2\text{TaF}_7$ .

To a large drop of a solution of the oxides in question in hydrofluoric acid or a hydrochloric acid solution to which  $\text{NH}_4\text{F} \cdot \text{HF}$  has been added, add potassium fluoride by Method I, page 31. Observe all the precautions so necessary when HF or its salts are employed as reagents.

Potassium fluotantalate is but sparingly soluble, whereas potassium fluocolumbate is easily soluble. Hence in mixtures the tantalum compound separates long before that of the columbium makes its appearance. In order that a separation of the latter can take place the preparation must pass almost to dryness.

$\text{K}_2\text{TaF}_7$  forms thin, slender, orthorhombic prisms with square or slightly oblique ends, grouped in irregular clumps (Fig. 143, page 205); they are weakly birefringent. The much more soluble columbium compound —  $\text{KCbF}$  — is also orthorhombic and when conditions are favorable separates in thin colorless plates and tablets. The monohydrated basic fluocolumbate is not likely to be met with if the preparation is moderately acid and the preparation is not heated.

In connection with this test see pages 43, 62, 180, 190.

#### B. Precipitation by Means of Sodium Hydroxide — NaOH.

*Compounds Formed* — Not definitely established.

When it is possible to obtain a sufficiently large quantity of hydrous



pentoxides to permit submitting them to separation methods and conversion into sodium columbate and tantalate, Cb can be satisfactorily differentiated from Ta by precipitation with NaOH. These salts are insoluble in NaOH solutions but readily soluble in distilled water when they are freshly prepared and not basic.

To the moderately concentrated aqueous test drop add a small drop of NaOH solution by Method I, page 31.

Sodium columbate is precipitated in colorless monoclinic acicular prisms, singly or in imperfect radiates and in clumps. The crystals exhibit parallel extinction. Thin, six-sided plates may also be present (Fig. 144, page 217). This monoclinic salt ( $\text{Na}_5\text{Cb}_6\text{O}_{19} \cdot 16 \text{H}_2\text{O}$  ?) is formed only when the NaOH is added in but slight excess. If in excess, a hexagonal salt is precipitated. If the mother liquor is decanted from the monoclinic crystals and the preparation recrystallized from hot water, colorless tablets and short, stout prisms are obtained (Fig. 145, page 217).

Sodium tantalate ( $\text{Na}_5\text{Ta}_6\text{O}_{19} \cdot 25 \text{H}_2\text{O}$  ?) forms colorless, thin hexagonal plates, tablets, rosettes, and disks.

It is obvious that properly to interpret precipitation tests obtained with NaOH it is essential to test a series of drops of varying concentrations with NaOH of different concentrations.

### DETECTION OF NITROGEN

In inorganic compounds nitrogen is met with as nitrides and as acid oxides of nitrogen united with various positive ions to form salts in which the nitrogen acids are present in various degrees of oxidation. For the detection of these acids, see pages 324-326.

For the identification of  $\text{NH}_3$  and amines, see page 74.

For N in cyanides, see page 330.

For N in complex cyanides, see page 332.

For N in thiocyanates, see page 332.

**Nitrogen in organic compounds** may be identified as follows. Into a tube of hard glass similar to that shown in Fig. 29, page 44, introduce a small amount of the finely powdered substance. Push down into the tube by means of an iron wire several tiny shavings of metallic sodium. The shavings should be in close contact with the powdered material. Heat the sodium very carefully so that in melting it comes in intimate contact with the material, then raise the temperature gradually until it is judged from appearances that a reaction has taken place and NaCN has been formed. Cool, cut off the portion of the tube containing the fused mass, crush, and extract with warm water; add to the solution a

little  $\text{FeSO}_4$ , heat almost to boiling, and filter, decant, or centrifuge. To the clear solution add  $\text{HCl}$  until distinctly acid. A dark-blue precipitate of Prussian blue indicates the presence of N in the compound tested.<sup>4</sup>

### DETECTION OF PHOSPHORUS

**Preliminary Treatment.** — If the material is soluble in water, add  $\text{HNO}_3$ , heat the preparation, and set aside to cool. When cold, test as below.

If the material is insoluble, fuse with  $\text{Na}_2\text{CO}_3$  and a little  $\text{KNO}_3$  so as to obtain a soluble phosphate. Dissolve in water, acidify with  $\text{HNO}_3$ , and evaporate to dryness, keeping the temperature below the boiling point. This material is dissolved in dilute  $\text{HNO}_3$  and tested for  $\text{PO}_4$ —.

**A. By Means of Ammonium Molybdate** —  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ .  
*Compound Formed* —  $(\text{NH}_4)_3\text{PO}_4 \cdot 10 \text{MoO}_3 \cdot \text{H}_2\text{O}$ .

To the dilute test drop add  $\text{HNO}_3$  until it is strongly acid. Prepare a drop or two of a moderately concentrated solution of the reagent; add thereto a drop of  $\text{HNO}_3$  (1 : 4) and warm the reagent mixture; no precipitate should form. If the reagent mixture remains clear, apply a drop, when cold, to the test drop by Method I. If a precipitate is formed in the reagent, add more  $\text{HNO}_3$  until the precipitate redissolves.

Ammonium phosphomolybdate separates slowly in the cold as a fine, granular, isotropic, yellow precipitate; later spherical grains appear and finally cubes and rounded octahedra. Warming the preparation hastens the reaction, but may cause the separation of other complex molybdates (Fig. 164, page 251).

This reaction, though sensitive, is not specific for phosphorus, for analogous molybdenum compounds are formed with silicon, vanadium, and arsenic, which are not distinguishable from the phosphomolybdate.

Behrens has suggested that the test be made in the cold, for the phosphomolybdate may then be identified because of its more rapid separation than is the case of the other complex molybdates. This requires a definite knowledge of concentrations in the test drop and the development of a high degree of discriminatory observation.

In spite of the fact that this reaction is not specific, it is the one that should be tried first, for it is sensitive, is subject to practically no interferences, and requires no care in the adjustment of conditions, other than the avoiding of too much  $\text{HNO}_3$ . Too much  $\text{HNO}_3$  may cause a

<sup>4</sup> Emich: *Lehrbuch der Mikrochemie*, p. 197.

precipitation of molybdic acid, but since this is white it cannot be mistaken for the yellow ammonium phosphomolybdate.

See Silicon, page 192.

### Experiment.

(a) Test a phosphate and an arsenate with ammonium molybdate.

#### B. By Means of Magnesium Acetate in Ammoniacal Solution.

*Compound Formed* —  $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$ .

Add to the test drop several large fragments of  $\text{NH}_4\text{Cl}$  and, when these are dissolved, the drop is made *strongly* ammoniacal with  $\text{NH}_4\text{OH}$ ; finally a moderately concentrated solution of  $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$  is added by Method I.

Orthophosphates yield a precipitate at once as a heavy granular mass. This apparently amorphous material is rapidly converted into large, six-pointed dendritic stars and irregular feathery fragments (Fig. 76, page 109). These skeleton crystals soon develop into characteristic orthorhombic prisms shaped like the roofs of houses, or they take a form resembling envelopes; if these are not fully filled out, they appear as H's or X's (Fig. 77, page 109).

The feathery stars, changing into prisms, are the most characteristic forms assumed by the reaction product. When non-characteristic crystals are obtained and doubt arises as to their nature, decant, dissolve the crystals in dilute  $\text{HCl}$ , and allow a drop of strong  $\text{NH}_4\text{OH}$  to flow into the  $\text{HCl}$  solution.  $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$  will be again precipitated and will probably now appear in crystals easily identified.

Arsenates form  $\text{NH}_4\text{MgAsO}_4 \cdot 6 \text{H}_2\text{O}$ , indistinguishable from the analogous phosphate and isomorphous with it. Ammonium magnesium phosphate separates from solutions that are weakly ammoniacal, but the corresponding arsenate requires a solution very strongly ammoniacal in order that the crystals can be made to appear. The difference is sometimes sufficiently marked to afford a clue as to which compound is present, or whether both are present.

To determine whether a crystalline precipitate is phosphate or arsenate, proceed as follows. Decant the mother liquor and wash the crystals thoroughly with water containing a little  $\text{NH}_4\text{OH}$ . This is usually readily accomplished since the crystals cling tenaciously to the glass and permit washing without becoming loosened from the object slide. Dissolve the insoluble residue in acetic acid (1:4). Add  $\text{AgNO}_3$  by Method I. Silver phosphate separates at once as a lemon-yellow, dense, curdy or granular precipitate. In a few minutes irregular crystallites appear, but the crystals obtained are rarely sufficiently well developed to offer a means of identification other than the color

(Fig. 198, page 337); but here too there may be uncertainty due to color variations. Silver arsenate is reddish-brown, or chestnut brown, or even a brownish-lavender. It crystallizes in a great variety of forms (see Silver, page 282), is readily soluble in  $\text{NH}_4\text{OH}$  and in  $\text{HNO}_3$ , from which it may be recrystallized in more characteristic forms than those in which it was originally precipitated (Figs. 196, 197, page 337).

For further data, see Detection of Anions, pages 346, 347.

#### Experiments.

(a) Test a phosphate and an arsenate with magnesium acetate and  $\text{NH}_4\text{OH}$ .

(b) Recrystallize the ammonium magnesium phosphate precipitate by dissolving in  $\text{HCl}$  and adding  $\text{NH}_4\text{OH}$ .

### DETECTION OF ARSENIC

Arsenic is ordinarily met with in four combinations: as the oxide  $\text{As}_2\text{O}_3$ ; as alkali arsenites corresponding to the formula  $\text{MAsO}_2$ , and complex arsenites of the heavy metals, of uncertain composition; as arsenates derived from orthoarsenic acid  $\text{H}_3\text{AsO}_4$ ; or as "metallic" arsenic and arsenides in alloys.

The attempt to identify the compound of arsenic should follow the detection of the element; the latter is most easily done by converting it into  $\text{AsH}_3$  and applying suitable tests for this gas.

In some combinations it may be necessary to separate the arsenic by heating in a hard glass tube in a current of chlorine.  $\text{AsCl}_3$  and  $\text{AsCl}_5$  can be thus expelled, absorbed, and tested for. Boiling materials with concentrated  $\text{HCl}$  may lead to a loss of arsenic as chlorides unless some element such as sodium or potassium is present to hold the arsenic as an arsenate; but even under these conditions there may be a loss.

It is well to bear in mind that arsenites are not readily oxidized to arsenates. The addition of  $\text{HNO}_3$  to some of them will cause a precipitation of crystalline  $\text{As}_2\text{O}_3$ .  $\text{As}_2\text{O}_3$  can be recrystallized from moderately strong  $\text{HNO}_3$ , but in the presence of nitrates of the alkalis the results are very poor.

#### A. Detection of Arsenic by Conversion into Arsine — $\text{AsH}_3$ .

The generation of arsine and its identification under the microscope by its action upon a fragment of colorless transparent silver nitrate can be conveniently accomplished by means of the apparatus illustrated in Figs. 150, 151, page 223.

The procedure is as follows: The side tube of the gas generator is first fitted with a tight plug of soft wood — *P*. Drop into the generator several shavings of bright arsenic-free zinc — *Z*. By means of a suitable capillary pipette introduce dilute, arsenic-free  $\text{HCl}$ . The acid will

occupy the space *A* as shown in Fig. 150. It will not flow down upon the zinc as long as the wooden plug *P* is tightly in place. A plug of absorbent cotton, which has previously been soaked in lead acetate and dried, is loosely inserted as shown at *C*. The capillary tube *T* containing a tiny crystal of  $\text{AgNO}_3$ , *S*, and a somewhat larger fragment of

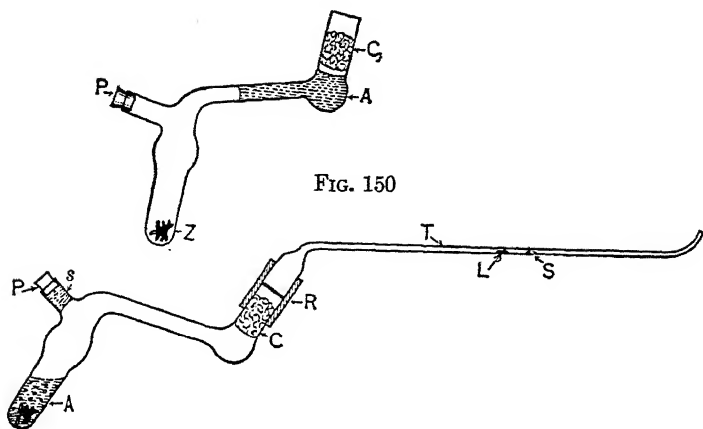


FIG. 150

FIG. 151

$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  *L*, is attached to the generator by the tightly fitting ring of rubber tubing *R*. The wooden plug *P* is removed for a moment and the acid allowed to flow down upon the zinc. A drop of water *s* is introduced into the side tube and the wooden plug reinserted. The water swells the wood and makes a gas-tight seal.

The apparatus is now in the position shown in Fig. 151, with *T* so held upon the stage of the microscope by means of the stage clips that the crystals *L* and *S* are in the field of a low-power objective. From time to time these crystals are examined to see if they change color. If, after a short time, *S* remains unchanged, clear, and colorless, the reagents are free from arsenic.

Carefully remove the wooden plug and, by means of a capillary tube, introduce several drops of a  $\text{HCl}$  solution of the material to be tested. Plug securely and watch the fragment of  $\text{AgNO}_3$  at *S*.

If arsenic is present,  $\text{AsH}_3$  is formed and the  $\text{AgNO}_3$  crystal turns first a lemon-yellow owing to the formation of a compound believed to have the composition  $\text{AgNO}_3 \cdot \text{Ag}_3\text{As}$ . The yellow color is fugitive and the crystal eventually turns black by reason of reduction to metallic silver. The lead acetate crystal remains unchanged unless  $\text{H}_2\text{S}$  is evolved. The lead-acetate cotton *C* should hold back all  $\text{H}_2\text{S}$  formed unless in excessive amount. The crystal serves, therefore, as an indi-

cator that no  $\text{H}_2\text{S}$  has passed over into the capillary tube  $T$ . This indication is essential since  $\text{H}_2\text{S}$  will turn  $\text{AgNO}_3$  crystals black because of the formation of black  $\text{Ag}_2\text{S}$ .

With antimony,  $\text{SbH}_3$  is obtained, which acts upon the  $\text{AgNO}_3$  in a manner similar to  $\text{AsH}_3$ , but a yellow compound is practically never seen, the crystal becoming black at once. A yellow color persisting for a few seconds can therefore generally be considered as proof that arsenic is present.

Phosphine turns the  $\text{AgNO}_3$  black at once; there is no transitional yellow-colored compound formed. The  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  is unaffected and does not hold back  $\text{PH}_3$ . If it is suspected that phosphine may be formed in the generator, it can be held back by placing below  $C$  a plug of absorbent cotton saturated with a  $\text{HCl}$  solution of cuprous chloride. When the crystal of  $\text{AgNO}_3$  turns black at once,  $\text{SbH}_3$  or  $\text{PH}_3$  has been formed or the evolution of  $\text{AsH}_3$  has been so rapid that the formation of the yellow compound may have been overlooked. In such an event,  $\text{AsH}_3$  should be sought by evolution through the action of metallic aluminum and  $\text{KOH}$ .

If only a very little antimony is present and much arsenic, a few bits of bright platinum wire may be introduced in contact with the zinc. Antimony is deposited upon the platinum as a velvety black coating.

To differentiate further between antimony and arsenic, the hydrides may be generated through the action of  $\text{KOH}$  on metallic aluminum; under these conditions  $\text{AsH}_3$  is alone evolved, and the antimony is deposited upon the aluminum and in part precipitated.

In place of  $\text{AgNO}_3$  at  $S$  a fragment of  $\text{HgBr}_2$  may be used, or a textile fiber soaked in  $\text{HgBr}_2$  and subsequently dried, or  $\text{HgBr}_2$ -paper can be employed. If a fiber is used, the internal diameter of the tube  $T$  must be such that the fiber practically fills it. Arsenic turns mercuric bromide red or brown; stibine behaves similarly.

The detection of very minute amounts of arsenic as  $\text{AsH}_3$  in the presence of iron is usually impossible, since the iron prevents the evolution of  $\text{AsH}_3$ .

**B. By Means of Ammonium Molybdate** —  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ .  
*Compound Formed* —  $(\text{NH}_4)_3\text{AsO}_4 \cdot 12 \text{MoO}_3 \cdot n \text{H}_2\text{O}$ .

The selection of the most satisfactory method of procedure for this test seems to depend more upon the nature of the material to be tested than is usual in microscopical qualitative analysis.

There is not only a diversity of opinions as to its value and interpretation, the nature of the compound formed, but also as regards the concentrations of acid, molybdate, and test drop.

The two procedures outlined below cover the widest range of applicabilities.

(1) The material to be tested is dissolved in HCl or aqua regia, evaporated to dryness, treated with HCl, and again evaporated to remove Si, Sb, Ta, and W. The residuum is extracted with dilute HCl, centrifuged, or the solution decanted from the insoluble material and evaporated almost to dryness. Add a tiny drop of water (if a precipitate results Sb, Bi are probably present; see below) and a larger drop of  $\text{HNO}_3$  (1 : 4). To the test drop thus obtained add the molybdate reagent (a  $1\frac{1}{2}$  per cent to 3 per cent solution in  $\text{HNO}_3$  (1 : 4) by Method I, page 31, carefully avoiding complete fusion of the two drops; warm gently, best upon a level metal plate (*P*, Fig. 1, page 5) supported about 4 cm. above the micro flame or electric heater (Fig. 3, page 8). The exposure to a gentle heat for the precipitation of the arsenomolybdate may require some little time. Being supported upon a metal plate insures less disturbance of the preparation and the separation of somewhat larger and better crystals. Moreover, by starting with a cold plate the heat is more gradually applied and the progress of the reaction can be better observed than if the preparation is held in the fingers high above the source of heat. The temperature gradient is important in interpretation of the reaction — ammonium phosphomolybdate separates at a much lower temperature than the arseno complex whereas the Bi and V complexes require higher temperatures and longer heating. The preparation must not be allowed to pass to dryness but should be removed at once upon the appearance of a precipitate, cooled thoroughly, and examined under the microscope.

Ammonium arsenomolybdate forms very small, highly refractive, light yellow isotropic granules, octahedra, cubes, and combinations. Skeleton forms are also almost always present (Fig. 136, page 197). If the preparation has been heated too rapidly and at too high a temperature, the crystals formed are so small as to be resolved with great difficulty. By transmitted light they appear to be colorless.

Phosphorus, vanadium, silicon, and germanium also form highly refractive, yellow isotropic granules, octahedra, and cubes which by transmitted light may appear to be colorless.<sup>5</sup>

Salts of bismuth and thorium treated as outlined above yield colorless precipitates mostly "amorphous," but always (?) a few isotropic octahedra are to be found. See Silicon, Method B, page 192.

If columbium, tantalum, and tungsten have not been removed, color-

<sup>5</sup> For a comprehensive study of heteropoly acids and their salts, see Illingworth and Keggin: *Jour. Chem. Soc.* 1935, I, 575.

less isotropic granules, octahedra, or skeleton crystals may interfere with or mask the reaction for arsenic.

Lead, silver, mercury, tin, antimony, bismuth should be removed before testing for arsenic by Method (1).

(2) This modification developed by M. N. Short<sup>6</sup> for the analysis of ore minerals has much in its favor because of its simplicity and relative freedom from interferences. It is equally valuable for the microscopical qualitative analysis of alloys.

The material to be analyzed is dissolved as in procedure (1) described above. The residuum obtained on evaporation is extracted with  $\text{HNO}_3$  (1 : 7). The repeated extracts are united, centrifuged if necessary, and a drop of the clear solution evaporated almost to dryness at a gentle heat. A drop of a  $1\frac{1}{2}$  per cent solution of ammonium molybdate in 1 : 7  $\text{HNO}_3$  is then added so as to cover completely the moist test drop. The preparation is again evaporated at gentle heat until it passes to dryness. One drop of 1 : 7  $\text{HNO}_3$  is applied to the dry residue (more if required) to dissolve the excess of molybdate reagent or other acid soluble salts. The tiny crystals of ammonium phosphomolybdate cling strongly to the object slide and permit decanting the solution and floating particles. The yellow arsenomolybdate has the appearance and properties described under procedure (1).<sup>7</sup>

**C. By Means of Cesium Chloride —  $\text{CsCl}$  — and Sodium Iodide —  $\text{NaI}$  — or Potassium Iodide —  $\text{KI}$ .<sup>8</sup>**

*Compounds Formed* —  $2 \text{AsCl}_3 \cdot 3 \text{CsCl}$  (?)

$\text{AsI}_3 \cdot 3 \text{CsCl}$

$\text{AsI}_3$

This test has little value for the identification of arsenic but becomes of major importance when dealing with materials containing antimony or bismuth because of the danger of confounding arsenic with either one of these two elements. (See Sb and Bi, Methods A and B, pages 230, 232.)

The unknown may be brought into solution by any of the procedures outlined in Methods 1 or 2, page 215.

Trivalent arsenic in dilute hydrochloric acid solutions yields no appreciable precipitate, but in strong  $\text{HCl}$  (1 : 2 to 1 : 3) arsenic triiodide is precipitated as a lemon-yellow granular mass from which, on standing, small yellow grains, disks, or hexagons may be formed.

<sup>6</sup> *U. S. Geological Survey Bulletin* 825, 156 (1931).

<sup>7</sup> For further details relative to the analysis of arsenical ore minerals, see Short: *op. cit.*, pp. 156–158.

<sup>8</sup> Short: *loc. cit.*, p. 158.



These crystals slowly become darker yellow, then orange, red, and finally so dark as to appear black by transmitted light.

Pentavalent arsenic, like trivalent, yields no precipitated iodide in dilute HCl; but, in strong acid, iodine is set free at once, and the arsenic is reduced to the trivalent condition and  $\text{AsI}_3$  is precipitated in dark-orange or red crystals. Rarely are yellow crystals obtained and then only for a very short time.

Antimony and bismuth under like condition also set free iodine but yield no precipitates in the cold.

Because of the uncertainty of obtaining characteristic crystals of  $\text{AsI}_3$  the test is of little value, but when combined with cesium chloride the reaction is materially improved.

If to a test drop containing arsenic acidified with HCl 1 : 5, or slightly stronger, a large fragment of cesium chloride is introduced at one edge of the drop, there will appear in a few seconds a white cloud or precipitate consisting of tiny, colorless, feebly polarizing, prismatic grains, square and rectangular plates and tablets, or more rarely six-sided plates. At a point on the circumference of the drop diametrically opposite the point of introduction of the CsCl, a large fragment of NaI or KI is introduced. Where the two reagents meet in the drop, cesium-arsenic chloriodide is formed and separates in thin yellow, orange, and red hexagonal plates (Fig. 137, page 197) and short, stout, orange hexagonal prisms; dark orange, slender, sharply pointed fusiform crystals are also present in great numbers, singly and in bristling clusters, accompanied by many curious, strongly birefringent, prismatic rods and grains. Iodine is liberated in blades, dendrites, rhombs, and aggregates black by transmitted light. (See Antimony and Bismuth, Method B, page 232.)

Three distinct compounds are therefore to be found in a preparation, all characteristic of arsenic but not specific for this element — colorless plates of the double chloride, deep red or brownish-red crystallites of triiodide and yellow to orange-red hexagons of the chloriodide.

The test drop should be dilute in arsenical ions, and free from nitric acid.

Sb, Bi, Pb, Se, Te, Tl, Hg, Cd, Ag, Sn, Cu may interfere with or mask the test. See pages 158, 203, 230, 257.

#### D. By Reduction to Metallic Arsenic and Subsequent Oxidation to Arsenic Trioxide — $\text{As}_2\text{O}_3$ .

The well-dried, finely powdered material is mixed with several times its volume of *anhydrous* potassium ferrocyanide. A portion of the mixture is placed in a subliming tube (Fig. 29, page 44),

and well tapped down so that all the mixture collects at the sealed tip of the tube.

Heat the mixture gently at first, gradually raising the temperature until it reaches a dull red and the glass begins to soften. The arsenical compound is reduced and "metallic" arsenic is deposited upon the walls of the tube as a blackish or brownish mirror; the latter type of mirror is the result of a partial oxidation of the arsenic.

Antimony yields a blacker or silvery mirror. Mercury gives tiny silvery spheres.

Certain compounds of carbon and compounds of sulphur may, under certain conditions, yield a deposit on the walls of the tube so closely resembling the brown "mirror" of arsenic as not to be distinguished therefrom by color alone.

To guard against misinterpretation, the sealed end of the tube is cut off and the mirror heated carefully, holding the tube inclined so as to induce a current of air to flow through the tube. Arsenic will be oxidized and will be sublimed as  $\text{As}_2\text{O}_3$  in the form of brilliant, highly refractive ( $n = 1.755$ ) isotropic octahedra. The crystals are soluble in KOH, forming  $\text{KAsO}_2$ , and are reprecipitated by  $\text{HNO}_3$  as well-developed octahedra. The potassium arsenite can be further tested as described below.

Arsenical compounds can be reduced to "metallic" arsenic by heating to boiling in HCl solution with a fragment of bright copper foil or copper wire. Arsenic colors the copper a smoky gray. Wash the coated copper with water and alcohol, dry very thoroughly, and drop into a subliming tube. On heating,  $\text{As}_2\text{O}_3$  is formed, which can be identified as described above or converted into  $\text{AsH}_3$  and tested as above. (See also Mercury, page 154.)

#### E. Distinction between Arsenites and Arsenates.

1. Strong  $\text{HNO}_3$  usually precipitates  $\text{As}_2\text{O}_3$  in glistening isotropic octahedra from concentrated solutions of arsenites, but no such precipitation takes place in concentrated solutions of arsenates.

2. A solution of silver nitrate (or better ammoniacal silver nitrate) reacts with an ammoniacal solution of arsenites, yielding lemon-yellow  $\text{Ag}_3\text{AsO}_3$  (?) as a curdy or granular precipitate which soon changes into minute acicular crystals; these crystals in turn grow into thin rods with notched ends or into long slender acicular prisms. On long standing oxidation is likely to take place, giving rise to crystals of silver arsenate. Silver arsenate is soluble in acids and also in strong  $\text{NH}_4\text{OH}$ ; hence the test may fail if the preparation is not examined at once, or if the drop and the reagent are too strongly ammoniacal.

Silver arsenate is precipitated in red, reddish-brown, or garnet-colored plates, dendrites, and skeleton crystals, the appearance and properties of which are discussed on page 282.

Silver arsenite cannot be confused with silver arsenate and there is little danger of a failure of the test. But silver arsenate resembles silver chromate and silver bichromate in color, and if in tiny crystals may be confused with these salts. The silver nitrate test for  $\text{AsO}_4$ — cannot be considered as conclusive unless  $\text{CrO}_4$  and  $\text{Cr}_2\text{O}_7$ — have been proved to be absent. In the recrystallization of  $\text{Ag}_3\text{AsO}_4$  in  $\text{HNO}_3$ , colorless octahedral crystals of  $\text{As}_2\text{O}_3$  may separate if  $\text{Ag}_3\text{AsO}_3$  is also present.

3. A strongly ammoniacal solution of  $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$  containing sufficient  $\text{NH}_4\text{Cl}$  to keep the magnesium in solution, when added to a solution of arsenates, gives a precipitate of  $\text{NH}_4\text{MgAsO}_4 \cdot 6 \text{H}_2\text{O}$ , isomorphous with  $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$ . The color, habit, and behavior, of the two compounds toward acids are identical. The descriptions given for the double phosphate on pages 76, and 130 apply equally well to the double arsenate.

Arsenites give a flocculent or granular precipitate but no crystals of the type obtainable with arsenates.

## DETECTION OF ANTIMONY AND BISMUTH

Antimony and bismuth are so closely related that their differentiation by microscopical tests is difficult and usually unsatisfactory when both are present in the material to be analyzed; but singly their identification is simple and rapid.

Tin is first removed by treatment with  $\text{HNO}_3$ . Much, sometimes all, the antimony separates with the  $\text{SnO}_2$  as  $\text{Sb}_2\text{O}_4$ . (See Tin, page 202.) Repeated extractions with  $\text{HNO}_3$  (1.20 sp. gr.) will not always remove the  $\text{Sb}_2\text{O}_4$ . It is usually best to redissolve the  $\text{SnO}_2$  and reprecipitate by evaporating with  $\text{HNO}_3$ . All  $\text{HNO}_3$  solutions and extracts are united and concentrated to small bulk or until the excess of free  $\text{HNO}_3$  is driven off. Add a tiny drop of water and view the preparation over a black background. A white turbidity, white precipitate, or white cloud indicates that antimony or bismuth, or both, are probably present. Stir the preparation so as to complete the hydrolysis, then add  $\text{HCl}$  cautiously until the basic nitrates are completely redissolved; but care must be used to avoid any more  $\text{HCl}$  than just sufficient to bring the antimonyl or bismuthyl salt into solution. Concentrate if necessary and *test as below*. When evaporating a low temperature should be employed for antimony chloride is volatile.

A. By Means of Cesium Chloride—CsCl—and Sodium Iodide—NaI.

*Compounds Formed*<sup>9</sup> — 2 SbCl<sub>3</sub>·3 CsCl (Hexagonal)  
                                   2 BiCl<sub>3</sub>·3 CsCl (Hexagonal)  
                                   BiCl<sub>3</sub>·3 CsCl (Orthorhom.)  
                                   2 SbI<sub>3</sub>·3 CsCl(?) (Hexagonal)  
                                   2 BiI<sub>3</sub>·3 CsCl(?) (Hexagonal).

To the moderately concentrated solution acidified with HCl add a large fragment of CsCl. (Method II, page 33.)

Antimony gives, at once, thin, colorless disks, with irregular edges, irregular six-pointed stars, rosettes, well-formed hexagonal plates, and elongated hexagonal plates. The hexagons usually show a system of straight or curving ribs extending from the center to the angles of the hexagons. (Fig. 146, page 217.)

If the CsCl has been properly applied in considerable excess, bismuth yields thin colorless rhombs, singly and in aggregates (Fig. 148, page 217); but, if the reagent is not in excess, hexagonal plates, stars, or disks are obtained, not to be distinguished from those formed by antimony (Fig. 149, page 217).

The rhombs of the 3 : 1 double salt are very weakly birefringent, usually appearing isotropic unless on edge. The hexagonal crystals of the 3 : 2 double salts appear isotropic when lying flatwise; on edge, and in prisms lying on a prism face, they are strongly birefringent.

Bismuth salts are thus readily differentiated from those of antimony, but in mixtures of antimony and bismuth hexagonal plates alone are obtained.

Conversion into orange or red iodo-compounds by introducing a fragment of KI into the test drop increases the sensitivity of the reaction. This reaction is slow, and time must be given for the development of the orange-yellow or orange-red compounds. The cesium iodo-bismuthate is darker in color than the iodo-antimonate and of a different shade; but this difference is not sufficiently marked to be dependable as a means of differentiation, for crystals of greatly varying thickness are

<sup>9</sup> Various formulas have been given for the reaction products. Behrens (*Anleitung*, p. 108) states that the double salts are 2 CsCl·SbCl<sub>3</sub>·2½ H<sub>2</sub>O and 2 CsCl·BiCl<sub>3</sub>·2½ H<sub>2</sub>O. Vermande: *Pharm. Weekblad* 55, 1131 (1918), gives the formulas above; the rhombic crystals of 3 CsCl·BiCl<sub>3</sub> are formed only if a large excess of CsCl is present. Ducloux: *Mikrochemie* 2, 108 (1924), gives a number of other formulas for different double cesium chlorides of antimony and bismuth, but apparently he has studied only the 3 : 2 salt. The work of Meloche and Clark: *Jour. Amer. Chem. Soc.* 52, 907 (1930) on 3 CsI·2 BiI<sub>3</sub>, which is hexagonal, confirms the analogous formula for the isomorphous 3 CsCl·2 BiCl<sub>3</sub>.

always obtained, and therefore the color intensities and hues of the hexagonal plates differ greatly according to their thickness.

In analytical practice, it is unwise to add the KI until the chloro-compounds have separated in sufficient amount to show the hexagons of the antimony salt or the rhombs of the bismuth salt, for the iodo-salts of both antimony and bismuth form hexagons but no rhombs. If the rhombs of cesium chloro-bismuthate have already been formed before the introduction of the iodide, they will be gradually colored since the iodo-salt forms a pseudomorph after the chloro-salt, and small, deep-colored hexagons will eventually appear, often as incrustations or pseudomorphs after the rhombs.

The compositions of the iodo-compounds are better established than those of the chloro-compounds; the weight of evidence appears to indicate that three molecules of CsI unite with two molecules of  $\text{SbI}_3$  or  $\text{BiI}_3$ . Iodine is almost always set free in performing this test, appearing as irregular skeleton fragments and prisms. Not infrequently well-developed rhombs are formed. These rhombs are practically opaque and are therefore black by transmitted light. Inexperienced analysts may mistake such crystals of iodine for very dark-colored crystals of the double iodo-salt of antimony or of bismuth.

It is essential that the KI be added to the test drop at room temperature, since, if warm,  $\text{BiI}_3$  may be thrown down as a dense, granular, brown or black precipitate.

Although antimony forms a red hexagonal triiodide,  $\text{SbI}_3$ , its separation in test drops under the conditions specified above has not yet been observed. However, the corresponding arsenic compound  $\text{AsI}_3$ , also hexagonal, may appear in test drops if very strongly acid (see Arsenic, Method C, page 226).

Polarized light affords a means of more easily differentiating between the rhombs of bismuth and the hexagons of antimony, for the rhombs are orthorhombic and birefringent, while the antimony salt is hexagonal and usually so orientated as to appear isotropic. Therefore any rhombs in the midst of hexagons can be readily found. Since bismuth forms both rhombs and hexagons, examination between crossed nicols should never be omitted.

Tin (see page 201) with CsCl gives very insoluble cubes or octahedra (as will silver), and if present will take up the CsCl first; hence the antimony or bismuth salt will not be formed until all the tin has been precipitated. In order to avoid this complication the tin should be removed with  $\text{HNO}_3$  before testing for antimony and bismuth. The excess of  $\text{HNO}_3$  must be fumed off; otherwise typical crystals cannot be obtained (Fig. 147, page 217).

The substitution of a mixture of RbCl and CsCl for pure CsCl in testing for antimony and bismuth often ensures a better formation of rhombs of the bismuth salt.

CsCl readily unites with the chlorides of many elements to form easily crystallizable double salts of solubilities such that they may separate under the conditions which obtain in this test.

Given the proper concentrations we may expect that the addition of solid CsCl may be followed by the separation of double cesium chlorides or insoluble simple chlorides of the following elements: Sb, Bi, Cu, Ag, Mg, Zn, Cd, Hg, Sn, Pb, Mn, Ni, Co, Fe, In, Ru, Rh, Pd, Pt. Some of these salts are, strictly speaking, not double chlorides, but cesium salts of complex ions. The most important of these chlorides have already been discussed on pages 152, 230.

Cadmium forms  $\text{CsCl} \cdot \text{CdCl}_2$ , bipyramidal twins of low solubility, which when first precipitated may be mistaken for octahedra of  $\text{Cs}_2\text{SnCl}_6$ . The corresponding Zn salt crystallizes in rhombs. There can be no danger of confusion, however, if the preparation is examined with polarized light, for the cadmium salt is anisotropic whereas the tin salt is isotropic. (See Cd, page 149.)

Under the conditions imposed in the test as indicated above, no cesium double chlorides will separate with the alkalis, nor with Ca, Sr, Ba, Al, Cr, (Vermande).

Many of the cesium double salts will be converted into iodo-compounds when KI is added, but in the majority of cases iodine is set free to such an extent as to mask the crystals which may separate.

#### Experiments.

- (a) Try the test on an Sb salt.
- (b) Test a Bi salt, using Method I, page 31. Repeat using Method II, page 33.
- (c) Try converting the chloro-salts of these two elements to the iodo-compounds.
- (d) Test mixtures of Sb, Bi, Cu, and Sn.

#### B. By Means of Tetraethylammonium Chloride — $(\text{C}_2\text{H}_5)_4\text{NCl}$ — and Potassium Iodide — KI.<sup>10</sup>

*Compounds Formed* —  $3(\text{C}_2\text{H}_5)_4\text{NI} \cdot 2\text{SbI}_3$   
 $3(\text{C}_2\text{H}_5)_4\text{NI} \cdot 2\text{BiI}_3$   
 $(\text{C}_2\text{H}_5)_4\text{NI} \cdot \text{SbI}_5$ .

The material is evaporated to dryness with  $\text{HNO}_3$ , and then extracted with HCl (1 : 2). The solution is diluted to about 1 : 7 and removed from any undissolved residue or precipitated chlorides (Ag, Pb,  $\text{Hg}^+$ ) by decantation, filtration, or centrifuging. A fragment

<sup>10</sup> Mason and Jones: *Ind. Eng. Chem. (Anal. Ed.)* 8, 428 (1936).

of potassium iodide is added to the solution. Oxidizing substances ( $\text{Cu}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{AsO}_4^{---}$ ) may liberate iodine, giving a yellow color in solution or a brown precipitate of iodine; Bi, Sb, As may give colored dissolved compounds. Insoluble iodides (Ag, Hg, Pb, Cu), or Se or Te, may be precipitated, at this point. The KI thus serves the purpose of a group reagent, and various identity tests may be made in the light of the precipitations occurring at this stage. To the solution containing KI, a fragment of tetraethylammonium chloride is added (Method II, page 33).

If solid reagents have been added in large excess, and in the presence of an oxidizing agent (even air), a yellow, relatively soluble compound may separate in their vicinity as rectangular plates or feathery four-armed stars; it is apparently a reaction product of tetraethylammonium chloride and iodine, but it need not be confused with any of the crystals obtained with metals.

Any precipitate is examined immediately, and also after standing; brief digestion may yield much larger crystals, or oxidation may permit a different product to form. If the crystals are too fine-grained, they may be recrystallized from dilute HCl solution by warming and allowing to cool. The tests for antimony and bismuth are relatively sensitive, and work best in dilute solutions of these ions. Slow mixing by diffusion of reagent and unknown beneath a cover-glass may sometimes be advantageous.

Antimony or bismuth, if trivalent, yield highly refractive granules, which may on standing coarsen sufficiently to be recognized as rhombohedra usually lying on pinacoid faces and resembling flattened octahedra (Figs. 152 and 153, page 235); this precipitate may also appear as hexagonal prisms and plates. The crystals of the tetraethylammonium antimony iodide are yellow, whereas those of the bismuth compound are of a darker amber or reddish-orange hue, sometimes almost brick-red. They can be differentiated with fair certainty, if separate; but, since they are isomorphous, mixtures of antimony and bismuth give crystals intermediate in color.

Oxidation serves further to distinguish between these metals, since antimony is much more readily rendered pentavalent than is bismuth. Preliminary evaporation with  $\text{HNO}_3$  accomplishes this, but even on standing a few minutes in the air enough  $\text{Sb}^{+5}$  is soon formed in the test drop to yield a different tetraethylammonium iodide compound, with distinctive crystals which appear as purple hexagonal plates, of low solubility (Fig. 154, page 235). Their spontaneous formation is shown in Fig. 153, page 235.

Pentavalent bismuth is not readily or completely produced by oxida-

tion with  $\text{HNO}_3$ , or by the air, and the dark-amber rhombohedral crystals of the trivalent bismuth compound will constitute the bulk of the precipitate. A few pink or brownish-red hexagonal plates may sometimes be formed; these are isomorphous with the corresponding antimony compound, and, if present, may prevent conclusive identification of a small amount of antimony in the presence of much bismuth.

Any ambiguity due to the above isomorphisms may be clarified by the utilization of additional specific reactions. The volatility of  $\text{SbCl}_3$  (b.p.  $220^\circ$ ) may be used to separate antimony from bismuth or other interfering substances. An  $\text{HCl}$  solution of the unknown is heated, and the evolved  $\text{SbCl}_3$  is collected in a hanging drop of tetraethylammonium chloride solution (by Method VIII, page 40) or simply by holding the slide carrying the hanging drop just above the solution being heated, as in Fig. 124, page 344, *Vol. I*). The test drop is cooled, and to it  $\text{KI}$  is added, to give the typical purple hexagonal crystals of the antimony compound. A small amount of  $\text{SnCl}_2$  in the solution to be "distilled" aids in the volatilization of  $\text{SbCl}_3$ .

Arsenic or arsenites may yield volatile  $\text{AsCl}_3$ , which, in high concentrations in the test drop, may give yellow hexagonal plates when the  $\text{KI}$  is added. These are relatively soluble and should not be confusing if the test drop is further diluted.

Bismuth is identified conclusively, even when present in solid solution in the crystals of the antimony compound, by treatment with sodium stannite. The test drop is evaporated to dryness, and the residue of pink to purple hexagonal crystals obtained with tetraethylammonium iodide is flooded with a moderately concentrated solution of sodium or potassium stannite. Bismuth is reduced to the element, yielding black pseudomorphs of the crystals or black grains and skeletal masses, if the crystals are mainly the antimony compound with a little bismuth in solid solution in them.

The stannite reagent may reduce lead compounds, but only very slowly at room temperature. However, bismuth catalyzes this reduction, so if lead has been found present the reduction should be tried on a lead salt alone, to enable the effect of bismuth to be compared with it.

The stannite reagent is prepared by adding to some  $\text{SnCl}_2$  solution enough  $\text{NaOH}$  or  $\text{KOH}$  to redissolve the white precipitate first formed; it should be free from specks of tin or other material, and its action should be tested on a precipitate known to contain bismuth. Examination by reflected light is essential, to differentiate between black metallic bismuth and white opaque hydrated oxides of antimony or other metals.

The reactions of elements that may cause interferences have been



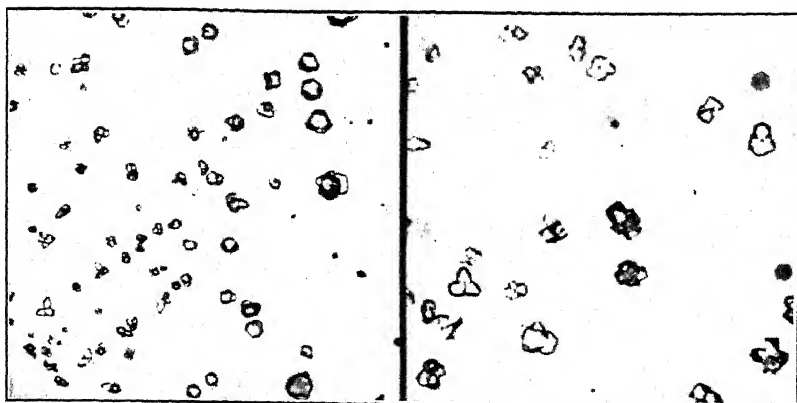


FIG. 152. Trivalent Antimony with Tetraethylammonium Chloride +KI. 200X

FIG. 153. Trivalent and Pentavalent Antimony with Tetraethylammonium Chloride +KI. 200X.

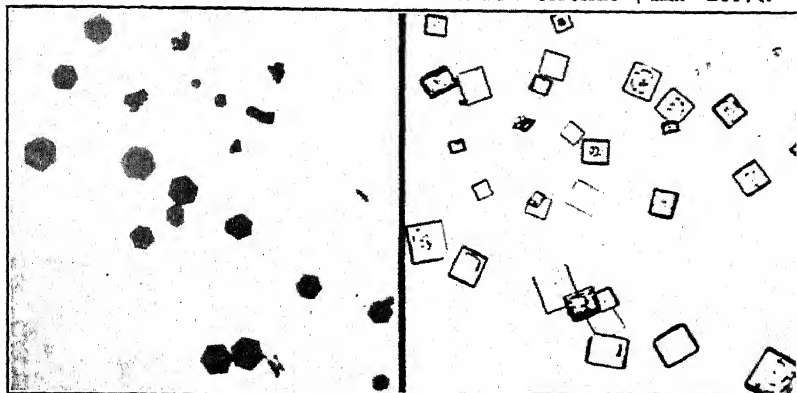


FIG. 154. Pentavalent Antimony with Tetraethylammonium Chloride +KI. 180X.

FIG. 155. Cadmium with Tetraethylammonium Chloride +KI. 50X.



FIG. 156. Tellurium with Cesium Chloride. 100X.

FIG. 157. Gold with Pyridine and Hydrobromic Acid. 100X.

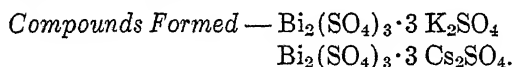
indicated above; in general these are not serious, and in some cases are useful as indicating the presence of other metals.

Lead is not completely precipitated by  $\text{Cl}^-$ , and addition of KI gives yellow hexagonal plates of  $\text{PbI}_2$ , soluble in excess. Neither these nor the colorless needles of the double salt  $\text{KI} \cdot \text{PbI}_2 \cdot 2 \text{H}_2\text{O}$ , which may form, should be confused with precipitates from Sb or Bi.

Tin ( $\text{Sn}^{++}$ ) in excess may yield large colorless octahedra of  $\text{K}_2\text{SnCl}_6$ , relatively soluble.  $\text{Sn}^{++}$  gives a precipitate of colorless to pale yellow rods and hexagonal prisms, and reduces  $\text{Sb}^{+5}$  to  $\text{Sb}^{+3}$ . This may hinder the formation of the characteristic purple hexagonal crystals, unless reoxidation by the air occurs. The preliminary evaporation with  $\text{HNO}_3$  will eliminate the tin, as  $\text{SnO}_2$ . Mercury ( $\text{Hg}^{++}$ ) gives red  $\text{HgI}_2$ , or yellow prismatic crystals of a double salt with excess KI. After reduction with  $\text{SnCl}_2$  metallic mercury may be separated, by decantation or filtration, from the solution to be tested. Copper, in addition to liberating iodine, may give a fine-grained precipitate of  $\text{CuI}$ .

Cadmium forms colorless rectangular plates (Fig. 155). Other metals may give "amorphous" or very fine-grained precipitates, of no distinctive character and not likely to interfere with the observation of the above crystalline precipitates.

### C. By Means of Potassium Sulphate — $\text{K}_2\text{SO}_4$ — or Cesium Sulphate — $\text{Cs}_2\text{SO}_4$ .



The material to be examined is first converted into sulphates by heating with a drop or two of sulphuric acid (1 : 1) until fumes of  $\text{SO}_3$  begin to be given off, but the preparation remains still moist. Tiny drops of water are successively added until the sulphates pass into solution. An excess is to be avoided; otherwise hydrolysis may result. If the solution is not clear, add a trace of nitric acid. To the test drop thus prepared add the cesium sulphate, or potassium sulphate. The bismuth-cesium sulphate separates in thin disks, six-pointed stars, and rosettes and in well-formed hexagons (Fig. 158, page 239).

Antimony yields no similar reaction; hence this test affords a means of differentiating between Bi and Sb.

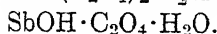
Under certain conditions not clearly understood both  $\text{K}_2\text{SO}_4$  and  $\text{Cs}_2\text{SO}_4$  may form crystals which may be mistaken for hexagons; but these alkali sulphates polarize strongly, whereas the hexagons (basal pinacoids) of the bismuth double sulphate appear isotropic.

The details of this test, precautions to be observed, and sources of

error have been discussed at length under Sodium, page 58, and Potassium, page 71.

**D. By Means of Potassium Bioxalate —  $\text{HK}(\text{C}_2\text{O}_4)$ .**

*Compounds Formed* —  $\text{KBi}(\text{C}_2\text{O}_4)_2 \cdot 7\frac{1}{2} \text{H}_2\text{O} (?)$



To the test drop, which should contain no more than just sufficient  $\text{HNO}_3$  to keep the antimony or bismuth in solution, add a moderately large fragment of  $\text{HK}(\text{C}_2\text{O}_4)$ .

With salts of antimony there is obtained a basic oxalate in the form of trichites at the periphery of the test drop, seldom in a zone near the fragment of reagent; but, with bismuth, acicular crystals and rhombs are to be found in a zone immediately surrounding the reagent. There are also a multitude of floating aggregates of plates and rosette-like groups.

If the preparation is warmed, the bismuth salt separates in tiny tetragonal octahedra. (See Alkaline Earths, page 114.) (Fig. 87, page 119.) Although the oxalate reaction is an excellent method for differentiating between antimony and bismuth in the case of simple salts of these metals, the test is valueless in mixtures since a number of other elements give crystals with  $\text{HK}(\text{C}_2\text{O}_4)$  so closely resembling those of antimony and bismuth as to be indistinguishable from them. (See page 120.)

**E. By Evolution as Stibine —  $\text{SbH}_3$ .** — In the presence of nascent hydrogen  $\text{SbH}_3$  is formed, and may be identified by passing the gas over a fragment of  $\text{AgNO}_3$ .  $\text{AsH}_3$  first turns the  $\text{AgNO}_3$  yellow, then black, but  $\text{SbH}_3$  turns the crystal black at once.

If the hydrogen is produced by the action of  $\text{HCl}$  and metallic zinc, both arsine and stibine are formed; but, when metallic aluminum and  $\text{KOH}$  are used to generate the hydrogen, only  $\text{AsH}_3$  is evolved. (See Arsenic, page 222.)

Bismuth forms no volatile hydride under the conditions of the test, and antimony may therefore be detected in the presence of bismuth.

A convenient form of apparatus for the performance of this test is shown in Fig. 151, page 223, and has already been described under Arsenic.

Differentiation between the blackening of the  $\text{AgNO}_3$  crystal by  $\text{SbH}_3$  and that brought about by  $\text{PH}_3$  can be accomplished by repeating the test with metallic zinc and  $\text{HCl}$ , but before the evolution starts a strip of platinum foil is introduced into the generator and placed in close contact with the pieces of zinc. Under these conditions, metallic

antimony is deposited as a velvety black coating upon the platinum and no  $\text{SbH}_3$  is evolved, but the evolution of  $\text{PH}_3$  (or  $\text{AsH}_3$ ) is unaffected. The black coating of antimony can be dissolved and subjected to confirmatory tests. The evolution of gas must be very slow.

#### F. Differentiation between Antimony and Bismuth by Conversion into Antimonyl Tartrate.

*Compounds Formed* — Potassium Antimonyl Tartrate,  $\text{KSbO} \cdot (\text{C}_4\text{H}_4\text{O}_6) \cdot \text{H}_2\text{O}$ ; or Barium Antimonyl Tartrate,<sup>11</sup>  $\text{Ba}(\text{SbO})_2 \cdot (\text{C}_4\text{H}_4\text{O}_6)_2 \cdot 2\frac{1}{2} \text{H}_2\text{O}$ .

The material to be tested is brought into solution as a chloride; concentrated at as low a heat as is practicable to drive off the excess of  $\text{HCl}$  but avoiding volatilizing any  $\text{SbCl}_3$ . Water or oxalic acid is added to precipitate  $\text{SbOCl}$  or  $(\text{SbO})_2\text{C}_2\text{O}_4$ . Decant, filter, or centrifuge. Dissolve the residue in tartaric acid, in which the corresponding bismuthyl salts are practically insoluble. Filter or centrifuge if necessary.

Concentrate the clear tartrate solution and divide it into two parts. To one portion add  $\text{KCl}$  by Method I, page 31, and allow the preparation to stand and undergo spontaneous evaporation. Examine at frequent intervals.  $\text{KSbO} \cdot (\text{C}_4\text{H}_4\text{O}_6) \cdot \text{H}_2\text{O}$  separates in colorless, highly refractive ( $\beta = 1.636$ ) tetrahedra, square, rectangular, and six-sided plates and tablets of the orthorhombic system. If no distinct crystals appear but a crust forms around the test drop, crush some of the crust and draw it across the drop, thus "seeding" the preparation (Fig. 159, page 239).

The second portion is diluted, acidulated with acetic acid, heated, and into the hot test drop a hot drop of a solution of  $\text{BaCl}_2$  or  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  is caused to flow.  $\text{Ba}(\text{SbO})_2 \cdot (\text{C}_4\text{H}_4\text{O}_6)_2 \cdot x\text{H}_2\text{O}$  is formed and separates in thin, glistening, symmetrical and elongated six-sided plates and tablets of the orthorhombic system. There is always a marked tendency to form imbricated aggregates.

The reaction of potassium antimonyl tartrate with silver nitrate, giving rise to the formation of large characteristic crystals of silver antimonyl tartrate,<sup>12</sup> is impracticable when dealing with mixtures, since the material to be tested almost invariably contains chlorides.

In the case of simple salts, either of these double tartrates of antimonyl are excellent and reliable for the identification of antimony and

<sup>11</sup> The formula of the barium salt is still in doubt. Groth gives  $\text{Ba}(\text{SbO})_2 \cdot (\text{C}_4\text{H}_4\text{O}_6)_2 \cdot \text{H}_2\text{O}$ , tetragonal (+) and  $\text{Ba}(\text{SbO})_2 \cdot (\text{C}_4\text{H}_4\text{O}_6)_2 \cdot 2\frac{1}{2} \text{H}_2\text{O}$ , orthorhombic (—). H. Behrens describes the salt as a dihydrated compound and W. Behrens also considers it as dihydrated, orthorhombic with weak negative birefringence.

<sup>12</sup> Kofler: *Arch. f. Pharm.* 256, 249 (1918).

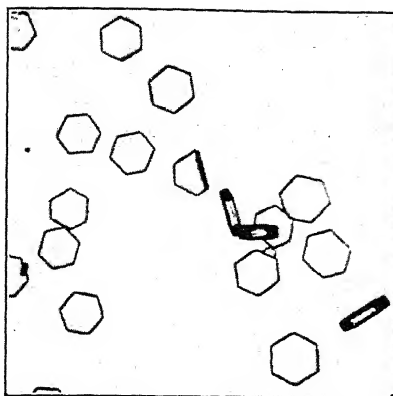


FIG. 158. Bismuth with Cesium Sulphate. 100X.

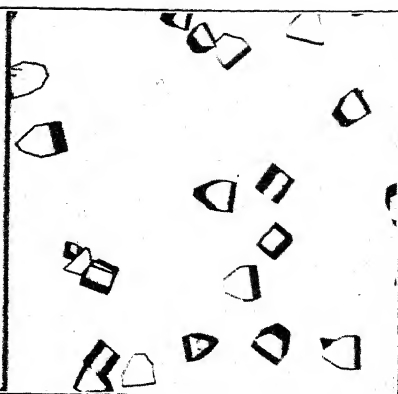


FIG. 159. Antimony Precipitated as Potassium Antimonyl Tartrate. 100X.

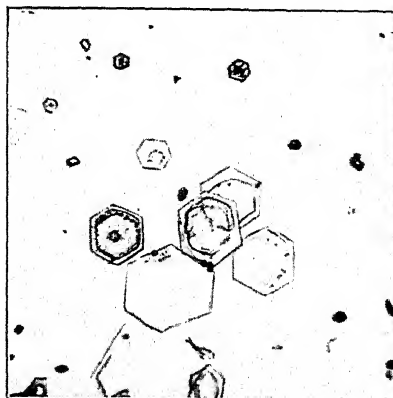


FIG. 160. Molybdenum ( $\text{MoO}_4^{++}$ ) with Thallous Nitrate. 100X.



FIG. 161. Tungsten ( $\text{WO}_4^{++}$ ) with Thallous Nitrate. 100X.

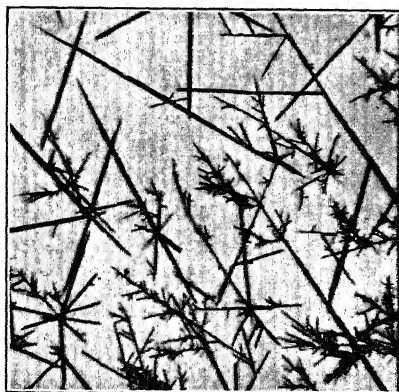


FIG. 162. Chromium ( $\text{CrO}_4^{++}$ ) with Thallous Nitrate. 100X.



FIG. 163. Manganese ( $\text{Mn}^{++}$ ) with Potassium Chromate. 100X.

its differentiation from bismuth, but unfortunately the tests fail when dealing with mixtures containing cations other than  $(\text{SbO})^+$  or  $(\text{BiO})^+$ .

Double tartrates corresponding to the general formula  $M^+\text{SbO}(\text{C}_4\text{H}_4\text{O}_6) \cdot \text{H}_2\text{O}$  are known where  $M^+$  may be  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $(\text{NH}_4)^+$ ,  $\text{Ag}^+$ , or  $\text{Tl}^+$ ; all are orthorhombic.

With bivalent elements the salts are  $M^{++}(\text{SbO})_2(\text{C}_4\text{H}_4\text{O}_6)_2$  or  $M^{++}(\text{SbO})_2(\text{C}_4\text{H}_4\text{O}_6)_2 \cdot n\text{H}_2\text{O}$ . Of the crystalline anhydrous double tartrates described are those of  $\text{Sr}^{++}$  (Hex.) and  $\text{Pb}^{++}$  (Hex.); and of the hydrated salts are  $\text{Ca}^{++}$  (Ortho.);  $\text{Ca}^{++}$  (Tetrag.?) ;  $\text{Ba}^{++}$  (Tetrag.) ;  $\text{Pb}^{++}$  (Mono.).

The double tartrates of antimonyl with monovalent and with bivalent cations form a long series of crystalline, *mixed*, double salts.

It is therefore obvious that the occurrence of any of these possible combinations can seriously interfere with the interpretation of a test for antimony, and should make clear the necessity of separating antimony from other elements before attempting to apply the tartrate test.

## CHAPTER VIII

### DETECTION OF THE ELEMENTS OF GROUP VI

O; Cr; Mo, W; U; S, Se, Te

The transition element of Group VI is oxygen; the primary subgroup consists of chromium, molybdenum, tungsten, and uranium, and the secondary subgroup of sulphur, selenium, and tellurium.

Considered merely from the point of view of microscopical analysis, Group VI may be divided into the following groups: O; Cr; Mo, W; U; S, Se, Te.

Considered in relation to their positions in the Periodic System, the elements in Group VI offer many highly interesting analogies. Many oxides are isomorphous with the corresponding sulphides. Most of the orthorhombic alkali sulphates are isomorphous with their corresponding selenates, chromates, molybdates, and tungstates; a similar relation holds for the orthorhombic  $\text{BaSO}_4$ ,  $\text{BaSeO}_4$ , and  $\text{BaCrO}_4$ . Silver sulphate is isomorphous with silver chromate and silver selenate. Similar isomorphous series are to be met with in many double salts, as for example in  $\text{K}_2\text{Mg}(\text{SO}_4, \text{SeO}_4, \text{CrO}_4)_2 \cdot 6 \text{H}_2\text{O}$ , and  $\text{Na}_3\text{Li}(\text{SO}_4, \text{SeO}_4, \text{CrO}_4, \text{MoO}_4, \text{WO}_4)_2 \cdot 6 \text{H}_2\text{O}$ ; in the "vitriols"; and in the "alums." Chromium shows horizontal analogies, for it forms "alums" isomorphous with those of manganese, iron, and vanadium (and all other "alums").

Although the instances of isomorphism are very numerous and striking in compounds of chromium, molybdenum, and tungsten and in those of sulphur and selenium, and between the first subgroup and sulphur and selenium, there are few cases of definitely established isomorphism of compounds of uranium or of tellurium with the other members of Group VI. Uranium is therefore easily detected, and tellurium likewise, providing selenium is not also present.

For the transitional element oxygen we have at present no known, direct microscopical qualitative test. It may of course be made to combine with hydrogen to form  $\text{H}_2\text{O}$  and the  $\text{H}_2\text{O}$  formed identified, but this requires a more or less complicated combustion apparatus and is impracticable for occasional tests only. Methods based upon liberating oxygen and its absorption by suitable reagents are also impracticable. Microscopical tests are also lacking for ozone and for hydrogen peroxide.

Such tests as may be employed, as for example KI and starch, benzidine, etc., are based upon recognition of oxidizing power, but none of them are specific for any one compound.

The identification of oxides and of basic salts must therefore be based upon their physical appearance and properties and upon their general chemical behavior. The presumption of the presence of oxides must rest largely upon negative evidence; that is, the analyst must reach a decision by elimination. This necessitates clear thinking founded upon a rather comprehensive knowledge of the chemical properties of the elements (or ions) found to be present and an ability to visualize the reactions that the combination in hand might be expected to exhibit under the conditions to which it is being subjected by the analyst. It is not possible to formulate any directions for a general plan of attack.

### DETECTION OF CHROMIUM

Chromium forms both chromous and chromic salts and chromates. The oxide  $\text{Cr}_2\text{O}_3$  acts as a weak base and does not form salts with weak acids. The oxide  $\text{CrO}_3$  comports itself as a strong acid.

Chromous salts are very unstable and easily oxidized, resembling ferrous salts, but are even less stable than the latter. They therefore rarely, if ever, occur in routine qualitative analysis.

All chromic salts are colored and occur in two modifications, one green, the other violet. It is now generally accepted that the green solutions contain complex ions and that we do not have simple  $\text{Cr}^{+++}$  ions present.<sup>1</sup> Such solutions may not give specific reactions for chromium, nor for the mineral acid present. The violet-colored salts behave normally. Both modifications are generally present in solutions.

Certain anhydrous violet-colored compounds, *e.g.*,  $\text{CrCl}_3$ ,  $\text{CrBr}_3$ ,  $\text{Cr}_2(\text{SO}_4)_3$ , are insoluble in both cold and hot water and also in dilute and in concentrated acids, but are readily soluble in water in the presence of  $\text{SnCl}_2$  (or if they contain traces of chromous salts).

The oxide  $\text{CrO}_3$  forms the chromate ion  $\text{CrO}_4^{--}$ , the dichromate ion  $\text{Cr}_2\text{O}_7^{--}$ , the trichromate ion  $\text{Cr}_3\text{O}_{10}^{--}$ , and several polychromate ions of somewhat uncertain composition. The salts of  $\text{CrO}_4^{--}$  are yellow; those of  $\text{Cr}_2\text{O}_7^{--}$  and more complex ions are red. No acid chromates are known.

Chromium forms no "basic acetate"; in this it resembles manganese and differs from iron and aluminum.

The addition of KOH or NaOH to solutions of chromic salts pre-

<sup>1</sup> See Weiser: *The Hydrous Oxides* (McGraw-Hill, New York, 1926), p. 81.

Urbain et S  n  chal: *Introduction    la chimie des complexes* (Hermann, Paris, 1913).



precipitates a grayish-green or grayish-violet hydrous oxide which *when freshly precipitated* is soluble in excess of the reagent (forming an alkali chromite) but is completely reprecipitated on boiling (thus differing from aluminum). The solubility in excess of the alkali in the cold may be very incomplete in the presence of many other metallic ions, *e.g.*,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Pb}^{++}$ ,  $\text{Ni}^{++}$ , and  $\text{Co}^{++}$  (Menchutkin). Aluminum cannot be satisfactorily separated from iron by KOH if chromium is present. Like iron, non-volatile organic acids prevent the precipitation of the hydrous oxide of chromium by alkalis.

$\text{NH}_4\text{OH}$  also precipitates a hydrous oxide, which even when freshly precipitated is only partially soluble in excess and is completely reprecipitated on boiling. The addition of  $\text{NH}_4\text{Cl}$  to a solution of an alkali chromite precipitates a hydrous oxide. The precipitate is soluble in  $\text{HCl}$ , a hydrous chloride being formed.

Chromium when present as compounds of  $\text{CrO}_3$  forms with chlorine a brown volatile liquid, chromyl chloride  $\text{CrO}_2\text{Cl}_2$ , boiling at about  $118^\circ$ .

The above brief outline of the chief chemical properties of chromium will serve as a foundation upon which to build our analytical procedures according to the nature of the problem in hand.

**Preparation of the Material for Analysis.** — (a) The material is a green or violet-colored, water-soluble salt or solution. Add a solution of KOH in excess until the precipitate first formed dissolves; boil. Decant, filter, or centrifuge; wash the precipitate and test for chromium as below.

(b) The material is insoluble in water. Boil with concentrated  $\text{HNO}_3$  to which small amounts of  $\text{KClO}_3$  are added from time to time. With few exceptions all chromium-containing compounds will pass into solution as chromates. Evaporate to dryness, carefully avoiding too high a temperature. Add  $\text{HNO}_3$  and again evaporate; repeat if necessary so as to drive off all chlorine compounds; but if the material is to be converted into  $\text{CrO}_2\text{Cl}_2$  the expulsion of  $\text{Cl}_2$  is undesirable.

(c) The material does not succumb to the treatment given in (b). Fuse the dry material with two or three times its volume of a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$  (2 : 1). Or fuse with sodium peroxide.

If chromium is present, the fused mass will be yellow when cold (unless the color is masked by iron, manganese, vanadium, or other metals). Dissolve in cold water and filter or centrifuge. Chromium will be in the filtrate; iron and aluminum will be in the insoluble residue.

In the fusion there is apt to be a partial decomposition of the  $\text{KNO}_3$ , and when the melt is dissolved in water the decomposition product reduces the yellow salt and the solution turns green. If the solution is distinctly green, complex ions will probably be formed and the subse-

quent reactions will be unsatisfactory. To obviate this difficulty it has been suggested that the fusing mixture consist of  $\text{Na}_2\text{CO}_3$  and  $\text{KClO}_3$ ; under these conditions all the chromium is oxidized to  $\text{K}_2\text{Cr}_2\text{O}_7$ . Great care must be used, for if mere traces of finely divided organic matter (dust) find their way into the molten  $\text{KClO}_3$  a violent explosion may result.

(d) Dry material containing chromium obtained by (b) or (c) is mixed with an equal volume of dry powdered  $\text{NaCl}$  and carefully heated in a crucible (Fig. 10, page 17) until perfectly dry. Pour over the residue about three times its volume of concentrated  $\text{H}_2\text{SO}_4$ . Cover the crucible with a small object slide carrying a tiny hanging drop of dilute  $\text{NH}_4\text{OH}$ . Clamp the cover-slide tightly in place and heat carefully, tilting the crucible slightly from side to side with a rotary motion so as to cause the heavy  $\text{CrO}_2\text{Cl}_2$  to rise. Allow to stand for a few minutes and heat again, raising the temperature to  $115^\circ$ – $118^\circ$ . Repeat. If  $\text{CrO}_2\text{Cl}_2$  has been formed and vaporized, the hanging drop will contain  $(\text{NH}_4)_2\text{CrO}_4$ . Evaporate the drop, dissolve in water, and test with  $\text{AgNO}_3$ . The compound  $\text{CrO}_2\text{Cl}_2$  can be obtained only when chromium is present as chromate, dichromate, etc., i.e., as compounds of the oxide  $\text{CrO}_3$ . The cation  $\text{Cr}^{+++}$  [ $\text{Cr}_2\text{O}_3$  (or  $\text{CrO}$ )] must first be converted to the anion ( $\text{CrO}_4^{--}$ ,  $\text{Cr}_2\text{O}_7^{--}$ , etc.).

(e) Separation of aluminum, iron, and chromium, Riggs' Method. To the solution add one-tenth its volume of  $\text{H}_2\text{O}_2$  and about one-tenth its weight of  $\text{NaOH}$ . Warm until effervescence ceases. Filter off or centrifuge the hydrous ferric oxide. Acidify the filtrate with acetic acid; hydrous aluminum oxide is precipitated. Filter or centrifuge. The clear solution contains the chromium as  $\text{Na}_2\text{CrO}_4$ .

### A. Detection by Means of Silver Nitrate — $\text{AgNO}_3$ .

*Compound Formed* —  $\text{Ag}_2\text{CrO}_4$  or  $\text{Ag}_2\text{Cr}_2\text{O}_7$ .

The reagent is added by Method I to the test drop of material treated as directed above and acidified with  $\text{HNO}_3$ . Dark red, highly pleochroic crystals appear at once in the form of thin plates and scales with very irregular outlines, X's with sharply inclined dendritic cross bars, unsymmetrical crosses, very acute rhombs, rectangular and elongated six-sided plates. Well-formed crystals are seldom obtained; skeleton and dendritic forms are the rule (Fig. 210, page 355). The salt formed is probably  $\text{Ag}_2\text{Cr}_2\text{O}_7$  when much  $\text{HNO}_3$  is used; otherwise  $\text{Ag}_2\text{CrO}_4$  (orthorhombic) is obtained.

$\text{Ag}_2\text{Cr}_2\text{O}_7$  and  $\text{Ag}_2\text{CrO}_4$  can be recrystallized from  $\text{NH}_4\text{OH}$  or from hot  $\text{HNO}_3$ . They can also be recrystallized from hot water, but the results are not so good; from neutral solutions the salt  $\text{Ag}_2\text{CrO}_4$ , and not

$\text{Ag}_2\text{Cr}_2\text{O}_7$ , separates. From the ammoniacal solution a complex salt is obtained containing one or more molecules of  $\text{NH}_3$ . This compound crystallizes in needles, skeleton crystals (X's), and aggregates resembling lichens.

Silver arsenate resembles silver chromate and bichromate in color (but not in pleochroism or in habit), (Figs. 196, 197, page 337). The differences are sufficient, however, to enable the skilled analyst to distinguish between them. Silver vanadate (pyrovanadate) is yellow or orange-colored (Fig. 142, page 205).

If much chlorine is present, as in testing the hanging drop in the  $\text{CrO}_2\text{Cl}_2$  separation method, the addition of solid  $\text{AgNO}_3$  (Method II) has much to recommend it. After all the chlorine has been precipitated as  $\text{AgCl}$ , the crystals of  $\text{Ag}_2\text{CrO}_4$  make their appearance and can be readily distinguished with even much  $\text{AgCl}$  present. It is better, however, to decant just before the silver chromate begins to separate.

If the amount of  $\text{CrO}_4^{--}$  is small, add a very little  $\text{H}_2\text{SO}_4$  to the test drop before the addition of the  $\text{AgNO}_3$ .  $\text{Ag}_2\text{SO}_4$  is formed, into which the  $\text{CrO}_4^{--}$  enters in solid solution (isomorphous mixture) rendering the crystals of  $\text{Ag}_2\text{SO}_4$  yellow or orange and pleochroic (Fig. 203, page 341). The sensitivity of the reaction is thus measurably increased, and the risk of mistaking it for arsenic or vanadium is obviated.

When the test drop contains ions forming compounds with silver which are insoluble in water acidified with  $\text{HNO}_3$ , so dense a precipitate may be formed as seriously to mask the reaction for  $\text{CrO}_4^{--}$ . They may also completely precipitate the silver, leaving none to react with the chromate; due allowance should be made for such a contingency and there should be a second addition of  $\text{AgNO}_3$ .

#### Experiments.

(a) Dissolve a small amount of a chromium alloy in concentrated  $\text{HNO}_3$  and  $\text{KClO}_3$  as directed above in (b). Test for  $\text{CrO}_4^{--}$  with  $\text{AgNO}_3$ .

(b) Precipitate a chromate with  $\text{AgNO}_3$ , from neutral solution. Repeat, having  $\text{HNO}_3$  present.

(c) Recrystallize  $\text{Ag}_2\text{CrO}_4$  from  $\text{NH}_4\text{OH}$ .

(d) Precipitate with  $\text{Ag}^+$  a chromate from a very dilute solution, in which a small amount of  $\text{SO}_4^{--}$  is present.

#### B. Detection by Means of Lead Acetate — $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{H}_2\text{O}$ .

*Compound Formed* —  $\text{PbCrO}_4$ .

To the test drop acidified with  $\text{HNO}_3$  add the reagent by Method I, page 31.

Lead chromate separates in a very finely divided granular state, and no definite crystal forms are observable. The precipitate must be viewed by reflected light, for the test is based upon its bright yellow

color, not upon crystal habit. Viewed by transmitted light, the bright yellow hue of the compound may not be recognized, especially when the precipitate is very small in amount.

This reaction for chromates should be regarded as supplementing and confirming the silver chromate test, for in the latter, as has been pointed out in A, the question always arises as to whether the crystals obtained with  $\text{AgNO}_3$  are those of chromate, arsenate, or vanadate.

Since lead chromate is bright yellow, whereas lead arsenate and lead vanadate are white precipitates, the  $\text{PbCrO}_4$  reaction may aid in clearing up any uncertainty in the silver test.

Strontium, barium, and zinc form yellow chromates of low solubilities in water, but since these chromates are soluble in  $\text{HNO}_3$  they are not likely to interfere with the reaction or to appear as precipitates. The same remarks apply with equal force to such of the rare earths as form difficultly soluble chromates.

#### Experiment.

(a) Precipitate  $\text{PbCrO}_4$  from very dilute solution.

#### C. Detection by the Chrome Alum Reaction.

*Compound Formed* —  $\text{CsCr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ .

The test is performed exactly as indicated for Aluminum, page 176, observing all the precautions there indicated.

A hydrous oxide of chromium is obtained by precipitation with  $\text{NH}_4\text{OH}$ , decanting, filtering, or centrifuging. It is of even more importance than in the case of aluminum that an excess of  $\text{H}_2\text{SO}_4$  shall be avoided. If the solution to be tested is yellow or red, acidify strongly with  $\text{HCl}$ , add a drop of alcohol, and heat to boiling. Chromates, dichromates, and polychromates are thus reduced, and a green solution of chromium chloride will be obtained which can be precipitated by  $\text{NH}_4\text{OH}$ .

Every effort should be made to induce the octahedral crystals of cesium chrome alum to grow of sufficient size to exhibit their characteristic grayish-violet color; for the test is not specific for chromium unless this can be done, but is common to a large group of "alum"-forming elements. (See page 169.) Nevertheless it is of value as a confirmatory test, particularly when obtained from a hydrous oxide precipitated from a green solution which, in turn, has been produced by the reduction of a yellow or red salt by alcohol. It is not always practicable to obtain crystals sufficiently thick to exhibit the color characteristic of chrome alum; confirmation may then be sought by means of a modification of a procedure suggested by Martini.<sup>2</sup> The preparation is allowed

<sup>2</sup> Martini: *Mikrochemie* 8, 143 (1930).

to evaporate almost to complete dryness and is then inverted over a small watch-glass or micro crucible containing a few drops of strong  $\text{NH}_4\text{OH}$ . If the crystals are chrome alum, they should darken in color and eventually become greenish or brownish before becoming completely broken down. The exposure must not be too long.

#### Experiments.

(a) Precipitate a hydrous oxide of Cr with  $\text{NH}_4\text{OH}$ , dissolve in a minimum of  $\text{H}_2\text{SO}_4$ , and test with  $\text{Cs}_2\text{SO}_4$ .

(b) Convert  $\text{CrCl}_3$  to the sulphate with  $\text{H}_2\text{SO}_4$ , and test with  $\text{Cs}_2\text{SO}_4$ . Complex ions will probably interfere.

(c) Confirm by  $\text{NH}_4\text{OH}$  treatment.

#### D. Miscellaneous Confirmatory Tests.

(a) Oxalic and oxalates give no precipitates with chromium compounds.

(b) Potassium ferrocyanide gives no precipitate.

(c) Potassium ferricyanide changes chromates into chromic salts. The same is true of potassium and of ammonium thiocyanates.

(d) Benzidine hydrochloride gives beautiful blue crystals with chromates. This reaction is not due to chromium but is the result of an oxidation of the benzidine. Blue crystals are obtainable with any oxidizing agent behaving in solution in the same manner as chromates.

(e) Chromates of the alkalis, of  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$ , and  $\text{Cu}^{++}$  are soluble in water. The chromates of  $\text{Tl}^+$  (Fig. 162, page 239),  $\text{Sr}^{++}$ ,  $\text{Zn}^{++}$ , and  $\text{Hg}^{++}$  are slightly soluble. The chromates of  $\text{Ag}^+$ ,  $\text{Ba}^{++}$ ,  $\text{Hg}^+$ ,  $\text{Pb}^{++}$ ,  $\text{Bi}^{+++}$ , and  $\text{Mn}^{++}$  are insoluble or nearly so.

In the presence of strong acids, chromates may be converted into bichromates.

Bichromates are precipitated as chromates by  $\text{Ag}^+$ ,  $\text{Ba}^{++}$ ,  $\text{Hg}^+$ ,  $\text{Pb}^{++}$ .

(f) Disodium phosphate precipitates chromium phosphate, insoluble in acetic acid.

#### DETECTION OF MOLYBDENUM AND TUNGSTEN

These two elements resemble one another so closely and they so frequently occur in association that their microscopical identification in mixtures is likely to be difficult and uncertain.

Since they are weak bases they are seldom met with save as molybdates, tungstates, acid complexes, and in alloys or ores.

Before applying identity tests it is generally necessary to convert the

material into alkali molybdates or tungstates, usually by fusion with alkalis, alkali carbonate-nitrate mixture, or sodium peroxide.

Alkali molybdates and tungstates are soluble in water without decomposition, whereas those of the other elements are insoluble or nearly so.

Both molybdenum and tungsten appear in compounds in a wide range of valencies, but commonly they are hexavalent.

Dilute HCl added to concentrated solutions of molybdates precipitates a white oxide soluble in excess of acid because of the formation of a complex (*e.g.*,  $\text{K}_2\text{MoO}_3\text{Cl}_2$ ). But with tungstates the precipitate which is obtained is insoluble in excess of acid. Boiling the preparation causes the precipitate to turn yellow.

If the white precipitate which is produced by the addition of acid to molybdates or to tungstates is dried and heated, in each case the oxide turns yellow (like  $\text{ZnO}$  and  $\text{TiO}_2$ ).

However, certain tungstates, which are sometimes called metatungstates, fail to yield a precipitate with HCl unless a great excess of acid is used and the preparation boiled for a considerable time; a yellow precipitate is then produced.

Both molybdenum and tungsten are very prone (like chromium) to form polyacids of varying composition.

Of the many complex salts of which molybdenum and tungsten are components, probably the most important from the standpoint of microscopical qualitative analysis are those known as salts of heteropoly acids. The other elements commonly associated with Mo and W in these acids are P, As, Ge, Si, Ti, B. The crystallizable salts of these very complex acids afford valuable identification tests in microscopical analysis for the cations and also the components of the anions.

There are no really satisfactory microscopical tests for molybdenum or for tungsten when these elements play the role of cations.

#### A. Detection by Means of Dipotassium Phosphate — $\text{HK}_2\text{PO}_4$ .

*Compounds Formed* —  $\text{K}_3\text{PO}_4 \cdot \text{MoO}_3 \cdot x\text{H}_2\text{O} (?)$

$\text{K}_3\text{PO}_4 \cdot \text{WO}_3 \cdot x\text{H}_2\text{O} (?)$ .

To the dilute test drop strongly acidified with  $\text{HNO}_3$ , a dilute solution of  $\text{HK}_2\text{PO}_4$  is added by Method I. The phospho-complex is almost instantly formed. If after a few seconds no precipitate appears, warm the preparation gently and set aside to cool for a few minutes. Examine with a magnification of about  $200\times$ . The precipitate is at first dense, heavy, and pulverulent; later the grains enlarge and appear more or less spherical; finally, very tiny isotropic octahedra are formed. The phosphomolybdate is yellow, but the phosphotungstate is white. When the



for differentiation appear to be more favorable, especially if the coating upon the reagent is studied.

Vanadates give a white precipitate with a yellow or brown coating on the reagent fragment. Beyond the granular zone, stars and rosettes appear, but only after the test drop has evaporated almost to dryness. The reagent fragment becomes covered with a mass of bristling crystals intermediate in form between  $\text{Ti}_2\text{MoO}_4$  and  $\text{Ti}_2\text{WO}_4$ , closely resembling the results obtained from a mixture of molybdates and tungstates.

The thallium reaction cannot be used to identify simultaneously molybdenum and tungsten when both are present, but can be used to advantage with pure tungstic or molybdic acids obtained by separating the two as described below.

Chromates give bright yellow  $\text{Ti}_2\text{CrO}_4$  in fine needles, very slender prisms, or irregular groups and radiating masses of fine needles. The reagent fragment becomes covered with bristling hairs which later develop into acicular crystals (Fig. 162, page 239).

It must not be overlooked that  $\text{TiNO}_3$  and  $\text{Ti}_2\text{SO}_4$  yield salts of low solubility with many simple anions and complex ions. (See Thallium, page 184; see also Uranium, page 253.)

**C. By Means of Pyridine Hydrochloride and Ammonium Thiocyanate<sup>3</sup>**—To the test drop, concentrated with respect to molybdates, add a drop of  $\text{HCl}(1 : 4)$  and a rather large mass of pyridine hydrochloride. Allow to stand for a few seconds, then add a large fragment of  $\text{NH}_4\text{SCN}$ .

Salts of molybdenum and salts of  $\text{MoO}_4^{--}$  yield yellow and brown oily drops, but no crystals appear to be formed even when the preparation passes to dryness.

Allow the preparation to stand and to evaporate to dryness. Extract the dry residue with absolute alcohol. The alcoholic extract on evaporation leaves a non-crystalline brown residue. Add a very tiny drop of water or breathe upon the preparation. If molybdenum is present, the brown compound is immediately changed into pink oily drops which, on standing, soon crystallize, giving rise to dendrites, plates, or tablets, X's, or to disks of radiating plates. These crystals are usually thin and appear to be faintly brownish when illuminated with ordinary transmitted light, but with polarized light they are extraordinarily pleochroic, the color changes being from a yellowish-brown or buff to an intense violet or purple (Fig. 165, page 251).

This reaction with pyridine hydrochloride, ammonium thiocyanate,

<sup>3</sup> Martini's reagent, modified. *Mikrochemie* 7, 30 (1929).



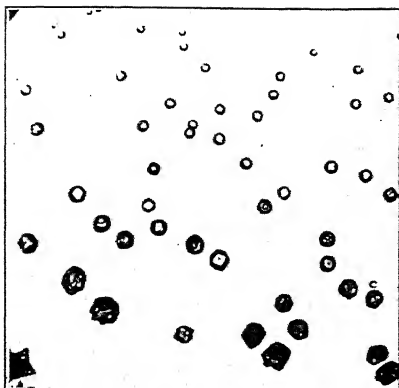


FIG. 164. Molybdenum ( $\text{MoO}_4^{--}$ ) with Dipotassium Phosphate. 200 $\times$ .



FIG. 165. Molybdenum ( $\text{MoO}_4^{--}$ ) with Pyridine Hydrochloride and Ammonium Thiocyanate. 200 $\times$ .

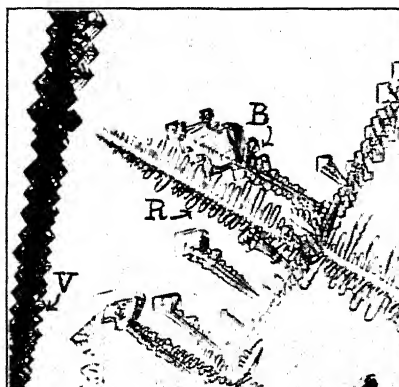


FIG. 166. Cobalt with Pyridine Hydrochloride and Ammonium Thiocyanate. 70 $\times$ .

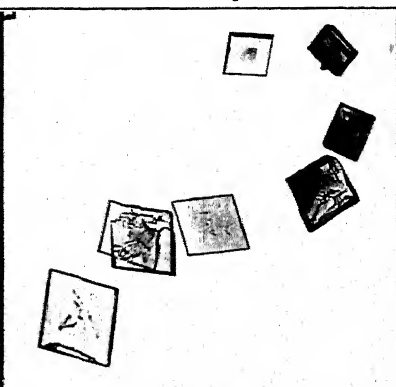


FIG. 167. Cobalt with Pyridine Hydrochloride and Ammonium Thiocyanate. 100 $\times$ .

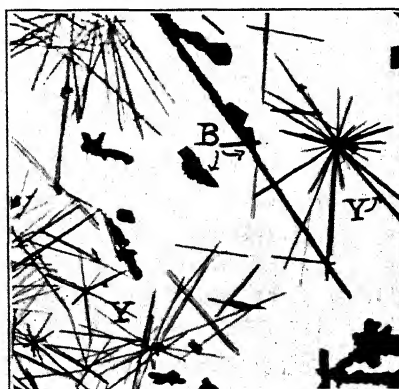


FIG. 168. Copper with Pyridine Hydrochloride and Ammonium Thiocyanate. 50 $\times$ .

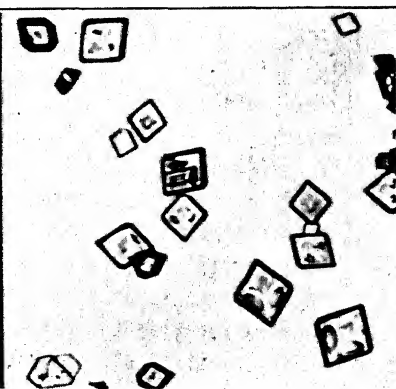


FIG. 169. Uranium ( $\text{UO}_2^{++}$ ) with Thallous Nitrate and Ammonium Carbonate. 200 $\times$ .

and polarized light, though not very sensitive, appears to be specific for molybdenum.

In hot weather or in a very hot room it is difficult to obtain characteristic crystals. Chilling the preparation by laying it upon a *cold* metal surface will induce crystallization of the pink oily drops.

Tungsten gives no reaction. Zirconium, titanium, vanadium (and tungsten) do not interfere. Vanadium salts and vanadates, however, usually give a faint bluish zone around the  $\text{NH}_4\text{SCN}$  fragment and also yield yellow and brown oily drops; but these droplets are not convertible by water into a colored, strongly pleochroic compound.

For reactions obtainable with other elements, see Cobalt, page 271.

#### D. Separations and Confirmatory Reactions.

(a) Separation of W from Mo and Te.<sup>4</sup>—The hydrous oxides obtained from sulphides or by other means are dissolved in aqua regia and are evaporated with concentrated HCl substantially to dryness. This dehydrates the tungstic acid and renders it insoluble in 2 N HCl. Boiling the residue with acid of this strength dissolves molybdenum, vanadium, and tellurium. From the solution tellurium can be precipitated by zinc and HCl.

(b) Dissolve the dehydrated  $\text{H}_2\text{WO}_4$  (obtained as described above) in  $\text{NH}_4\text{OH}$ , evaporate almost to complete dryness, cover with a drop or two of  $\text{SnCl}_2$ ; a flocculent, deep-blue compound is obtained —  $\text{W}_2\text{O}_5 \cdot x\text{WO}_3$ .

(c) To the HCl extract from the method of separation (a), add KSCN and metallic zinc. If molybdenum is present, the solution turns a deep red, not destroyed by  $\text{H}_3\text{PO}_4$  (distinction from iron). Tungstates give a similar reaction.

(d) To the solution acidified with HCl add a fragment of  $\text{K}_4\text{Fe}(\text{CN})_6$ .

Mo. The fragment becomes surrounded by a deep-brown, jelly-like colloidal mass; at a distance from the reagent the brown compound becomes curdy, and yet farther away, granular.

W. Usually little action until warmed, then a brown colloid is formed, less jelly-like than in the case of Mo.

The brown compound is soluble in  $\text{NH}_4\text{OH}$  and also in NaOH. Distinction from U and Cu.

(e) Solutions containing Mo or W, acidified with HCl and treated with metallic Zn, give a blue solution; but in the case of Mo the solution does not remain blue, but finally becomes brown.

<sup>4</sup> Noyes and Bray: *Qualitative Analysis for the Rare Elements* (Macmillan, New York, 1927), p. 74.

## DETECTION OF URANIUM

The element uranium, although falling in the same vertical group as molybdenum and tungsten, has little in common with them micro-analytically, but presents certain analogies with chromium. Uranium functions chiefly as a base and forms few compounds in which it acts as an acid. The uranates are weak compounds which are easily decomposed.

The tests for uranium are based upon the assumption that either uranyl nitrate or uranyl acetate has been produced and is present in the test drop.

#### A. Detection by Means of Sodium Acetate and Zinc Acetate.

*Compound Formed* —  $\text{Na}(\text{C}_2\text{H}_3\text{O}_2) \cdot \text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot x\text{H}_2\text{O}$ .

At the corner of an object slide dissolve in dilute  $\text{HC}_2\text{H}_3\text{O}_2$  a very little  $\text{NaC}_2\text{H}_3\text{O}_2$  and about twice as much  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ . Mix thoroughly by stirring and carefully evaporate to dryness so as to obtain a thin uniform film. Place near the dry film a drop of the material believed to contain uranium, acidify with  $\text{HC}_2\text{H}_3\text{O}_2$ , mix, and draw the solution in a narrow streak across the dry film. (Method III, page 35.)

If uranium is present, there will be formed tetrahedra of sodium uranyl acetate and octahedra-like, monoclinic, polysynthetic twins of sodium zinc uranyl acetate. The characteristics of these two salts have been discussed at length under Sodium, page 51 (Figs. 30, 32, 33, page 53).

The reaction is peculiar to uranium and is subject only to the sources of error due to the precipitation of uranium in insoluble form, as stated under Sodium.

#### B. Detection by Means of Thallous Sulphate — $\text{Tl}_2\text{SO}_4$ — in a Solution Containing Ammonium Carbonate.

*Compound Formed* —  $2 \text{Tl}_2\text{CO}_3 \cdot (\text{UO}_2) \text{CO}_3$ .

This reaction, according to H. Behrens, is much more sensitive than that given above. We have, however, found it always difficult to obtain, save when dealing with comparatively pure uranium products and under rather carefully controlled conditions. Moreover, the crystals are very tiny and require a high power to resolve them.

To the solution to be tested,  $\text{NH}_4\text{OH}$  is added and the precipitate thus produced is separated by filtration or by the centrifuge, and is dissolved in a strong solution of ammonium carbonate. To this ammoniacal solution a fragment of thallous sulphate or thallous nitrate is added. As in substantially all cases where  $\text{Tl}_2\text{SO}_4$  or  $\text{TlNO}_3$  are used as reagents,

the reagent fragment first becomes coated with a drusy layer of the double salt, and it is only after a few minutes that a zone of free crystals can be observed at a short distance from the reagent. The tiny crystals are probably orthorhombic and take the form of rhombic plates and more or less irregular three-, four-, and six-sided tabular crystals or crystalline grains (Fig. 169, page 251).

There appears to be some confusion as to the true nature of the salt which separates. Some investigators have ascribed to it the formula  $\text{Ti}_2\text{SO}_4 \cdot (\text{UO}_2)\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ,<sup>5</sup> but since crystals of identical habit are obtained whether  $\text{Ti}_2\text{SO}_4$  or  $\text{TiNO}_3$  is used as the reagent it seems reasonable to consider that H. Behrens' formula  $2\text{Ti}_2\text{CO}_3 \cdot (\text{UO}_2)\text{CO}_3$  is correct.

Since the crystals are minute and their habit not readily discerned, and since thalious compounds are precipitated by so many different ions, the confirmatory test suggested by Behrens should never be omitted. To this end, decant the mother liquor and flood the precipitate with a solution of  $\text{K}_4\text{Fe}(\text{CN})_6$  in acetic acid. If the precipitate consists of a salt of uranium, a brown precipitate results. This should make the test conclusive, providing copper has been proved to be absent.

### C. By Means of Quinoline and Ammonium Thiocyanate.

The test is performed as suggested under Method C, pages 194–198; Figs. 130, 131, page 195.

### Miscellaneous Reactions.

(a) With oxalic acid or oxalates: Separation of  $\text{UO}_2 \cdot \text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$  in very pale yellow orthorhombic prisms and plates, the latter thin, rectangular, or square (see page 120).

(b) With alkali hydroxides or ammonium hydroxide, basic uranates are precipitated  $[(\text{UO}_2)_2\text{O} \cdot (\text{OM})_2]$ , insoluble in excess of the reagents, but readily soluble in  $(\text{NH}_4)_2\text{CO}_3$ .

### DETECTION OF SULPHUR, SELENIUM, AND TELLURIUM

Free sulphur is met with in the analytical laboratory in several allotropic forms: orthorhombic crystals with a m.p.  $112.8^\circ$ ; monoclinic crystals, m.p.  $119^\circ$ ; both soluble in  $\text{CS}_2$ ; a waxy amorphous condition only partly soluble in  $\text{CS}_2$ ; finely divided sulphur precipitated from certain salts by  $\text{HCl}$  and insoluble in  $\text{CS}_2$ ; and a second form of finely divided sulphur, also precipitated from another class of salts by  $\text{HCl}$ , which in this case is soluble in  $\text{CS}_2$ .

<sup>5</sup> W. Behrens: *Tabellen*, p. 203.

H. Behrens: *Anleitung*, p. 123.

If  $\text{CS}_2$  is employed for the extraction of material believed to be sulphur and the extracted matter is to be submitted to tests for identification, it is essential that a blank test be made upon the solvent to make sure that it does not leave a residue of sulphur on evaporation. Most commercial samples of this solvent contain sulphur in solution.

Material believed to be sulphur may be identified by conversion into  $\text{H}_2\text{SO}_4$  by oxidation with aqua regia or exposure to bromine vapor (Method IX, page 41). The excess of oxidizing agent if driven off by gentle heat, the residue dissolved in water, and tested for  $\text{SO}_4^{--}$  with calcium acetate (see Calcium, Method B, page 106). Selenium yields calcium selenate isomorphous with calcium sulphate.

Hydrogen sulphide may be recognized by its odor. Absorbed in a hanging drop of dilute KOH and a drop of a solution of sodium nitroprusside added, an intense purple color is produced. This reaction is obtainable in alkaline solution with loosely bound sulphur only. Sulphides which are not alkaline do not respond to the test.

Since most selenites and selenates are isomorphous with their corresponding tellurites, tellurates, and sulphates, it is always necessary to prove the absence of selenium and often that of tellurium before there can be any certainty regarding the presence of sulphur compounds, and *vice versa*.

The detection of selenium and tellurium is based upon the ease with which they are reduced to the "metallic" state, and that when finely divided their colors are very different.

Most tellurium compounds differ in their chemical behavior sufficiently from those of sulphur and selenium so that there is little danger of confusion; but between certain compounds of sulphur and selenium there is such a close resemblance as to necessitate care on the part of the analyst if he wishes to avoid errors.

The material to be tested for selenium and tellurium is first treated with concentrated nitric acid or with aqua regia. The excess of the oxidizing agents is removed by gentle heat. The residue may then be tested by Method B, page 256, or HCl (1 : 4 or 1 : 5) added and the identification made by Method A, page 255. Heating with HCl without previous oxidation is often inadvisable as Se or Te may be lost as  $\text{H}_2\text{Se}$  or  $\text{H}_2\text{Te}$  or volatilized as chlorides.

#### A. Detection of Selenium by Means of Hydroxylamine Hydrochloride — $\text{NH}_2\text{OH} \cdot \text{HCl}$ .

*Compound Formed* — Se.

To a drop of the NaOH or HCl solution of the material to be tested several fragments of citric acid are added, and the preparation stirred

until the citric acid has dissolved. If a precipitate occurs add more acid until a clear drop has been obtained. A fragment of hydroxylamine hydrochloride is now added. If selenium is present there will form around the fragment of reagent a brown ring; eventually finely divided, bright red selenium is precipitated. The preparation must be viewed by reflected light. The reaction proceeds quite slowly; the preparation, therefore, should be allowed to stand for at least an hour before deciding that selenium is absent.

Whether the precipitate be red, brown, or black, it consists of selenium, for it has been shown<sup>6</sup> that in the presence of citric acid no tellurium is precipitated. Traces of selenium in the presence of tellurium can be detected by this method.

In the absence of any precipitation of selenium the preparation can be tested for tellurium by adding a drop or two of HCl (1 : 4) and a fragment of metallic zinc. Tellurium is precipitated in a dense black granular or flocculent zone about the zinc, but not clinging to the fragment as "trees" do.

If the material is suspected of being a salt of acids of sulphur, selenium, or tellurium, the test can be applied direct, but in very complex material it is wise to precipitate the selenium or (and) tellurium by means of SO<sub>2</sub> in HCl, in cold, or warm but not hot, solutions.

The necessity for an examination by reflected light has been mentioned above. This is essential since in concentrated solutions the reagent often becomes covered with a dense white coating, which, as it falls off and becomes peptized, appears brown by transmitted light if sufficiently finely dispersed, or if the white precipitate scatters the light it will appear black; in either case leading to a false conclusion on the part of the analyst.

### B. Detection of Selenium and Tellurium by Means of Hydroquinone<sup>7</sup> — C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>.

*Compound Formed* — Se; Te.

The material to be tested is dissolved in concentrated HNO<sub>3</sub> and evaporated to dryness at the corner of an object slide. The dry residue is covered with one or more drops of moderately concentrated H<sub>2</sub>SO<sub>4</sub> and heated until fumes of SO<sub>3</sub> appear. Treat again with H<sub>2</sub>SO<sub>4</sub> and decant from any insoluble precipitate. The decanted solution is evaporated until SO<sub>3</sub> fumes are formed. Cool the preparation. (Before the preparation has completely cooled, it should be examined for crystals of 2 TeO<sub>2</sub>·SO<sub>3</sub> which may have been formed.) Place a drop of

<sup>6</sup> Lehner and Kao: *Jour. Amer. Chem. Soc.* 47, 2454 (1925).

<sup>7</sup> Putnam, Roberts, and Selchow: *Amer. Jour. Sci.* 15, 257 (1928).

a saturated solution of hydroquinone in concentrated  $\text{H}_2\text{SO}_4$  adjacent to the test drop and cause it to flow into the test drop. *Warm gently.* Selenium is precipitated brown or red, depending upon particle size. This reaction is specific for Se.

Under the conditions of the test as given above, tellurium is not reduced until the temperature is raised to the point when  $\text{SO}_3$  fumes are formed. If therefore, no selenium has been precipitated, the preparation is heated until  $\text{SO}_3$  is evolved. Cool and examine under the microscope. Tellurium separates in very slender, black acicular crystals, in sheaves, irregular bundles, and in aggregates forming crosses or radiating masses.

If much selenium is present, the selenium precipitate obscures the crystals of tellurium. Both selenium and tellurium are, however, precipitated separately and usually can be distinguished one from the other. Decanting after the separation of the selenium and before fuming off the  $\text{SO}_3$  is always advisable.

When tellurium is present in appreciable amount, it is possible to obtain an identity test for this element prior to the addition of the hydroquinone. If the cooled test drop is examined, there will be seen masses of thin colorless plates grouped in malformed irregular rosettes with many petals; there are also formed bundles of plates on edge resembling sheaves of acicular crystals. The compound is probably  $2\text{TeO}_2 \cdot \text{SO}_3$ ;<sup>8</sup> its appearance is characteristic and seems to be specific for tellurium. The refractive index of this compound is but slightly greater than that of concentrated sulphuric acid. Unless great care in adjusting the illumination of the preparation is exercised, the presence of crystals may be completely overlooked. Under certain conditions bismuth salts heated with concentrated  $\text{H}_2\text{SO}_4$  give rise to crystals which may puzzle the inexperienced analyst. It is essential that the preparation be examined promptly under the microscope before it has become thoroughly cold, for the crystals redissolve in the water absorbed from the air by the  $\text{H}_2\text{SO}_4$ .

### C. Detection of Tellurium by Means of Cesium Chloride — $\text{CsCl}$ .<sup>9</sup>

*Compound Formed* —  $\text{Cs}_2\text{TeCl}_6$ .

Solutions of  $\text{TeO}_2$ , tellurites, and oxidized tellurides, in strong  $\text{HCl}$  (1 : 2 to 1 : 5), yield at once with  $\text{CsCl}$  a copious precipitate consisting of light yellow, clear, regular octahedra and thin, three-sided and six-sided yellow plates (distorted crystals, see *Vol. I*, Fig. 115, page 306).

<sup>8</sup> Putnam, Roberts, and Selchow: *loc. cit.*

<sup>9</sup> Behrens-Kley: *op. cit.*, p. 154.

Short: *op. cit.*, p. 165.

Although the compound formed —  $\text{Cs}_2\text{TeCl}_6$  — is soluble in moderately strong  $\text{HCl}$ , poor preparations cannot be recrystallized satisfactorily. The compound is decomposed by water.

The best results are obtained when the concentration of  $\text{Te}$  in the test is high and the reagent is applied by Method II, page 33.

The test drop should have an acidity of  $\text{HCl}$  not less than the equivalent of a 1 : 5 acid and a large fragment of  $\text{CsCl}$  introduced at the center of the drop. Under these circumstances there is immediately formed around the dissolving fragment a dense granular precipitate, black by transmitted light, consisting of very tiny yellow octahedra. In a zone just beyond this granular mass, well-formed, moderately large, clear, transparent, light yellow octahedra separate (in appearance similar to the crystals shown in Fig. 43, page 69, but somewhat less refractive). At the outer edges of this zone of octahedra, large, thin, three-sided and six-sided yellow plates are formed (Fig. 156, page 235).

In "thin" test drops, relatively low in  $\text{Te}$ , the plates are likely to predominate to the almost complete exclusion of typical octahedra.

Selenium does not give this reaction; neither do salts of telluric acid —  $\text{H}_2\text{TeCl}_4$ .

Minerals are best opened up by treatment with concentrated  $\text{HNO}_3$  added in several repeated small volumes, evaporating just to dryness after each addition, but carefully avoiding heating at too high a temperature. The residue is extracted with  $\text{HCl}$  (1 : 5), the extracts concentrated by evaporation to insure a high  $\text{Te}$  content, and into the test drop thus obtained a fragment of  $\text{CsCl}$  is introduced. If the oxidation has not been carried too far, the  $\text{Te}$  should have been converted into a derivative of  $\text{TeO}_2$ , with little or no higher oxidation to  $\text{TeO}_3$ . However, it may happen that tellurates have been formed, particularly if but little  $\text{Te}$  was present in the unknown. If no crystals of  $\text{Cs}_2\text{TeCl}_6$  are found, test the preparation for tellurates. Tellurates can be reduced to tellurites by treating the  $\text{HCl}$  solution with a fragment of alkali sulphite. Evaporate carefully to dryness to agglutinate the sulphur set free, extract with  $\text{HCl}$  (1 : 5), filter or centrifuge if still turbid, and test with  $\text{CsCl}$ . A slight amount of turbidity or opalescence does not appear to mask the reaction.

When bromine is present, the light yellow octahedra of the chlorotellurite acquire a darker shade of yellow and may even become orange. If in doubt as to their character, add a fragment of  $\text{KI}$  to the preparation. The crystals should turn brown and slowly disintegrate to a brown amorphous powder if they contain  $\text{Te}$ .



**Miscellaneous Reactions of Selenium and Tellurium.**

(a) Solutions of selenium and tellurium compounds in HCl are reduced by  $\text{SO}_2$  to Se and Te if  $\text{SO}_2$  is in large excess; but, if  $\text{SO}_2$  is insufficient to cause complete reduction, selenium monochloride is formed, and can be distilled off in a pure state.<sup>10</sup>

This separation can be practiced in the micro crucible with a hanging drop.

(b) Selenium and tellurium are strongly electronegative; elements more electropositive than Se or Te will therefore reduce their compounds and precipitate them in a finely divided condition — red, brown, or gray in the case of Se; gray or black in the case of Te.

(c)  $\text{FeSO}_4$  in *concentrated* HCl at room temperature reduces selenates but not tellurates, but Te is precipitated if *dilute* HCl is used; the same is true with  $\text{Na}_2\text{SO}_3$ .

(d)  $\text{SnCl}_2$  in HCl solution reduces both Se and Te if the preparation is warmed. (See Mo and W.)

(e)  $\text{SeO}_2$  sublimates at  $200^\circ$ , but  $\text{TeO}_2$  fuses at a red heat and is volatilized only at high temperatures.

(f) Selenic acid reacts to form crystalline plates with benzidine hydrochloride  $(\text{C}_6\text{H}_4\text{NH}_2)_2\text{H}_2\text{SeO}_4$ .<sup>11</sup> Sulphuric acid forms a similar compound but much more soluble. Tellurous and telluric acids yield no visible reaction nor does selenious acid. It is essential that the reagent be present in high concentration.

(g) See KI as reagent, page 159.

<sup>10</sup> Lehner and Kao: *Jour. Amer. Chem. Soc.* 47, 769, 2454 (1925).

<sup>11</sup> Kretow: *Chem. Ser. B. J. angew. Chem.* 5, 634 (1932).

## CHAPTER IX

### DETECTION OF THE ELEMENTS OF GROUP VII

#### F; Mn; Cl, Br, I

Group VII consists of the transitional element fluorine; the subgroup chlorine, bromine, and iodine; and the elements manganese and rhenium.

There are but few analytical analogies in Group VII that need occupy our attention.

Fluorine stands practically alone. It will be met with in the form of fluorides or fluorine-containing complexes. From these the fluorine is liberated by strong acids, and in the presence of silicon and sodium forms characteristic sodium fluosilicate whose behavior and properties have been discussed under Sodium, page 62. (See also Detection of Anions.)

Manganese resembles its horizontal analogue iron in Group VIII, especially in its bivalent sulphate and double sulphates. Its analogy to chlorine is well marked in the isomorphism of alkali permanganates and alkali perchlorates; advantage of this is taken in the detection of  $\text{ClO}_4^-$  and also of members of the potassium group.

Chlorine, bromine, and iodine form a triad of probably the most closely related elements in the Periodic System. Not only are they closely related in the habit of their many commonly met with salts, but their analytical behavior is such as to require great care when dealing with mixtures in which two or more of the halogens are present.

The halogen salts of the alkalis comprise the vast majority of the isotropic salts with which the analyst comes in contact.

Since the detection of chlorine bromine, and iodine involves the detection of halides and halates, the consideration of the analytical procedures to be followed will be found under the designation of these anions. (See pages 373-387.)

#### DETECTION OF MANGANESE

**A. Conversion into Permanganic Acid by Means of Sodium Bismuthate —  $\text{NaBiO}_3$ .**

*Compound Formed —  $\text{NaMnO}_4$ .*

Dissolve the material in concentrated nitric acid. Evaporate this solution to dryness; add more  $\text{HNO}_3$  and again evaporate. If the unknown is insoluble in  $\text{HNO}_3$ , dissolve in strong or fully concentrated

HCl or in aqua regia and evaporate to dryness; then evaporate to dryness with  $\text{HNO}_3$ . Should the presence of organic matter be suspected or that of difficultly decomposable reducing substances, it is best at this point to heat the dry residue until it begins to turn brown or black.

The final residue obtained as above is heated with  $\text{HNO}_3$  (1 : 5 to 1 : 7), and to the cooled solution sodium bismuthate is added a very little at a time, stirring after each addition and allowing a few seconds interval between each addition. A pink, purple-red, or violet-red color indicates manganese. No other cation yields a similar reaction.

It sometimes happens that manganese dioxide is formed rather than permanganic acid. In such an event add to the acid solution the smallest possible fragment of sodium thiosulphate. Let the preparation stand for a short interval and repeat the treatment until substantially all the dark-colored precipitate has been dissolved, but avoid an excess of thiosulphate. To the milky liquid add several drops of  $\text{HNO}_3$  (1 : 5), warm gently, cool, and treat with sodium bismuthate as before. A pink or purple-red color should now result if manganese is present. The bismuthate must always be applied in slight excess; but, if in great excess, its dark color may so completely mask that of very small amounts of permanganate as to render interpretation difficult. Under these circumstances it is wise to centrifuge or filter the solution through an asbestos plug in the filter tube and view the clear liquid against a white background. Or, if the final test drop is not too thick with precipitate, a little KCl may be added, followed by a drop of perchloric acid. Characteristic pink or red crystals are formed (see Potassium, Method B, page 68).

#### B. Conversion into Permanganic Acid by Means of Ammonium Persulphate — $(\text{NH}_4)_2\text{S}_2\text{O}_8$ — with Silver Nitrate as Catalyst.

The preliminary treatment of the unknown should be the same as that outlined in Method A, but if halogens are present there should be more treatments with concentrated  $\text{HNO}_3$  in order that they may be in a great measure driven off. The residue is then dissolved in  $\text{HNO}_3$  (1 : 5) and a minute fragment of silver nitrate added, the preparation stirred vigorously, so as to cause the white precipitate to agglutinate, and centrifuged. There should have been added only the slightest excess of silver. Small fragments of not too old<sup>1</sup> ammonium persulphate are added to the clarified drops, stirring after each addition.

<sup>1</sup> Putnam, Roberts, and Selchow: *Amer. Jour. Sci.* 15, 261 (1928), have shown that ammonium persulphate soon loses its efficacy as an oxidizing agent for this test. Blank tests should therefore always be made upon a manganese salt in order to verify the proper condition under which the reagents at hand will yield unequivocal reactions for very small amounts of manganese.

Finally the preparation is heated until the maximum color has been developed; this ordinarily requires a temperature raised almost to the boiling point. Cool quickly, add a few drops of dilute  $\text{HNO}_3$ , centrifuge, and examine the tube against a white background. A pink, purple-red, or violet-red color indicates manganese.

*Caution: In both Methods A and B, the nitric acid used must be perfectly colorless and free from lower oxides of nitrogen.*

**C. By Means of Oxalic Acid —  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ .**

*Compound Formed —  $\text{MnC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$ .*

This reaction is applicable only to manganous salts in a moderately pure state, but under favorable conditions it is sensitive and characteristic.

The most reliable procedure is as follows. Prepare upon an object slide a dry film of oxalic acid, or, better, one of acid potassium oxalate (see Method III, page 35). Place, adjacent to the reagent, a drop of the moderately dilute neutral (or at the most only faintly acid) solution of the material to be tested.

The preparation must be thoroughly cooled before the solution is drawn across the oxalate film. Under these conditions the trihydrate separates in long thin prisms and in radiates built up by the crossing of twinned prisms having acute or truncated ends. These *radiates* are characteristic of manganese (Fig. 89, page 119). When not formed, the test is in doubt. The prisms are birefringent and exhibit parallel extinction and brilliant polarization colors; they are commonly accompanied by highly refractive crystalline grains and pseudo-octahedra. Under the microscope  $\text{MnC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$  appears to be colorless but in bulk is faintly pink.

At room temperatures the trihydrate very slowly transforms into a monotropic dihydrate —  $\text{MnC}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ .<sup>2</sup>

The solubility of the trihydrate is increased in the presence of oxalic acid. Excess of ammonium salts (including ammonium oxalate) and more than strong traces of acids or alkalis prevent the separation of crystals. However, the preparation may be slightly acid with acetic acid or slightly ammoniacal without seriously affecting the reliability of the test.

The test may be masked by elements forming insoluble or difficultly soluble oxalates, particularly those to be found in Group II and in Group VIII. (See page 120.)<sup>3</sup>

<sup>2</sup> Coltman: *Jour. Ind. Eng. Chem.* 16, 606 (1924).

<sup>3</sup> See also Schoorl: *Beiträge*, p. 107.

Wagenaar: *Pharm. Weekblad* 49, 14 (1912); *Chem. Abs.* 6 (1), 724 (1912).

**Experiments.**

(a) Test, as above,  $\text{MnSO}_4$ . Then try the addition of a drop of  $\text{H}_2\text{C}_2\text{O}_4$  to a test drop, by Method I.

(b) Try the effect of free acids upon the test.

**D. By Means of Potassium Chromate —  $\text{K}_2\text{CrO}_4$ .**

*Compound Formed* — Manganous chromate of variable composition.

To the neutral or alkaline, moderately concentrated test drop apply the reagent  $\text{K}_2\text{CrO}_4$  by Method II, page 33. Tiny granules at first appear which grow into groups, masses, sheaves, and radiating aggregates of yellowish-brown, strongly pleochroic, acicular crystals (Fig. 163, page 239).

The test drop should be neutral or slightly alkaline, and more than a mere trace of free  $\text{HNO}_3$  retards the separation of the crystals and greatly alters the crystal habit. Instead of fine acicular crystals, dendritic masses of stout, yellowish-brown prisms are obtained. Other strong mineral acids have a like effect.

$\text{K}_2\text{Cr}_2\text{O}_7$  applied as above gives no crystalline precipitate.

$\text{Ag}^+$ ,  $\text{Pb}^{++}$ ,  $\text{Tl}^+$ ,  $\text{Hg}^+$ ,  $\text{Hg}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Sr}^{++}$  mask or interfere with the reaction.

The reaction should be obtained at room temperatures without heating. Hot solutions yield very different products and the formation of basic chromates for the most part, red or black in color.<sup>4</sup>

**Experiments.**

(a) Test a drop of  $\text{MnSO}_4$  with  $\text{K}_2\text{CrO}_4$ ; with  $\text{K}_2\text{Cr}_2\text{O}_7$ .

(b) Repeat the test in a solution slightly acid with  $\text{HNO}_3$ .

**Miscellaneous Reactions for Manganese**

(a) *By Fusion with Alkali Carbonates.*—The fusion can be performed upon platinum foil or in a tiny platinum cup.

Manganese fused with alkali carbonates gives an alkali manganate intensely green in color. The green color is even more marked when the melt is moistened with water. This color reaction is doubtless the most sensitive and specific of the tests at our command.

Often by carefully acidifying the alkaline solution with  $\text{H}_2\text{SO}_4$  the green manganate  $\text{Na}_2\text{MnO}_4$  is converted into pink permanganate  $\text{NaMnO}_4$ , and this in turn is decomposed with the precipitation of a hydrous oxide of manganese.

Iron and chromium may completely mask the reaction; for this reason it is better practice first to precipitate the manganese as a hydrous oxide and use this precipitate for the fusion test.

<sup>4</sup> See Wunschendorff and Valier: *Compt. rend.* 197, 584 (1933).

**Experiment**

(a) Oxidize  $\text{MnSO}_4$  to manganate, by fusion. Acidify, and precipitate  $\text{KClO}_4$  in the solution.

(b) *Precipitation of Manganese as  $\text{Mn}_3\text{O}_4$ (?)*. — The precipitation of a brown or black oxide, probably hydrated, can generally be accomplished by several methods. The solution to be tested is made strongly ammoniacal,  $\text{H}_2\text{O}_2$  added, and the mixture boiled. A brown hydrated peroxide is precipitated. In the absence of cobalt (and nickel) this reaction is characteristic of manganese. Cobalt gives a precipitate indistinguishable from that of manganese. Filter or centrifuge; dry the precipitate and fuse with alkali as above.

The precipitation of an oxide of manganese by  $\text{H}_2\text{O}_2$  is a valuable means of separating manganese from other elements, both for the purpose of identifying manganese and also to remove manganese before testing for other ions with whose detection manganese might interfere.

Manganese can also be separated by adding  $\text{KClO}_3$  to a solution in moderately concentrated  $\text{HNO}_3$  and boiling; dark brown  $\text{MnO}_2$ (?) is precipitated, which can be filtered off, or centrifuged, and a confirmation test for manganese applied. Cobalt may yield a similar brown precipitate.

(c) Disodium phosphate in ammoniacal solutions precipitates  $\text{NH}_4\text{MnPO}_4 \cdot 6\text{H}_2\text{O}$  in an amorphous condition. If allowed to stand for some time and the concentration conditions are just right, crystals may be found which are identical in appearance and isomorphous with the magnesium compound of the same formula (see Mg. Method B, page 130). But the conditions required for the formation of crystals of recognizable habit are so seldom present in microscopical qualitative analysis that this test is of doubtful value for the identification of manganese. However, when magnesium is present, there is always the likelihood of isomorphous mixtures, and the reaction becomes therefore important. Make the preparation strongly ammoniacal and add a drop of  $\text{H}_2\text{O}_2$ . If Mn (or Co) is present, the colorless crystals should turn brown; the oxidation is slow.

(d) Evaporate to dryness a concentrated test drop of the unknown so as to obtain a strictly neutral preparation. Place at the center of the residue a small fragment of ammonium molybdate, upon which in turn place a small drop of water. Set the preparation aside for half an hour or more. Yellow and dark orange, strongly dichroic plates and prisms of a manganese molybdate separate in a crystalline crust in a zone around the ammonium molybdate fragment or at the edges of the dried drop. No other cation gives a similar reaction (Staples).

## CHAPTER X

### DETECTION OF THE ELEMENTS OF GROUP VIII

Fe, Co, Ni; Ru, Rh, Pd; Os, Ir, Pt  
(Cu, Ag, Au)

In Group VIII are found the elements forming the ends of the three long horizontal periods of the Periodic System and therefore a group of elements whose properties are in a large measure transitional between Groups VI and VII and Group I.

In Group VIII a basic character is again in the ascendancy, in most cases completely submerging acidic properties. Of the acidic properties there remain but the vestiges to be found in the composition of some of the oxides and in the formation of unstable alkali ferrates, ruthenates, and osmates (*e.g.*,  $\text{K}_2\text{FeO}_4$ ,  $\text{K}_2\text{RuO}_4$ ,  $\text{K}_2\text{OsO}_4$ ). These compounds correspond to the analogous molybdates, tungstates, chromates, and manganates, and in general comport themselves in like manner. Of these acidic forms, the only ones likely to be encountered in qualitative chemical analysis are ruthenium red and osmic acid.

In Group VIII the close analogies between the elements are to be found in the horizontal lines rather than in the vertical, and the subgroups which interest the analyst are subdivision horizontally instead of vertically; that is to say that iron, cobalt, and nickel resemble each other more closely than do iron, ruthenium, and osmium. So, too, rhodium behaves more like palladium than like cobalt or iridium, and palladium forms salts which react more like those of rhodium than like similar salts of nickel or platinum; the resemblance to nickel is, however, apparent in the formation of a difficultly soluble glyoxime.

Vertical analogies hold to a limited degree, however, and the analyst is confronted with a dual grouping not marked in the other main groups of the Periodic System. He must also bear in mind the transitional character of the members of Group VIII as exemplified in the series Cr, Mn, Fe, Co, Ni, Cu; Mo, Ru, Rh, Pd, Ag; and W, Os, Ir, Pt, Au.

Another characteristic not to be forgotten is that the similarities in the properties of the elements in the horizontal long periods hold for the next horizontal long period above or below, but there is little analogy with the nearest elements in the horizontal short periods.

Group VIII taken as a whole is characterized by the marked tendency

with which its members unite with acidic elements to form *complex anions*. In these stable complexes the specific reactions of the individual elements are lost and a characteristic reaction for the complex ion must be sought, or the complex must be completely destroyed by ignition, fusion, or the action of a powerful decomposing agent.

The salts of the elements of Group VIII offer many striking analogies with those of other elements in the horizontal long periods. These analogies can be readily understood by reference to tables of optical properties. For example, monoclinic  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  is isomorphous with monoclinic  $\text{CoSO}_4 \cdot 7 \text{H}_2\text{O}$ . Triclinic  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ , if crystallized in the presence of  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ , becomes monoclinic. Orthorhombic  $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$  in the presence of monoclinic  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  becomes monoclinic. On the other hand, monoclinic  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  in the presence of orthorhombic  $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$  becomes orthorhombic. A great variety of solid solutions are thus possible, and it is probably not far from the truth if we say that the sulphates of iron, cobalt, nickel, manganese, magnesium, and zinc can form isomorphous mixtures. All of these elements also form monoclinic, hexahydrated, double sulphates of the general formula  $M_2\text{SO}_4 \cdot N\text{SO}_4 \cdot 6 \text{H}_2\text{O}$ , where  $M$  is an element of the potassium group and  $N$  one of the elements just referred to.

The bivalent compounds of iron, cobalt, and nickel corresponding to the formulas  $\text{Fe } X_2$ ,  $\text{Co } X_2$ , and  $\text{Ni } X_2$  closely resemble like compounds of chromium, manganese, and copper, and also to a certain degree those of magnesium, cadmium, and zinc.

$\text{Fe } X_3$  is analogous to  $\text{Al } X_3$ ,  $\text{Cr } X_3$ , and  $\text{Mn } X_3$ , and in most cases the salts are isomorphous. A further resemblance of  $\text{Fe}^{+++}$  to  $\text{Al}^{+++}$ ,  $\text{Mn}^{+++}$ , and  $\text{Cr}^{+++}$  is seen in the formation of ferric alum.

Both iron and cobalt unite with other elements to form complex ions, but this property is much less marked in nickel. A further similarity between iron and cobalt is to be found in the formation of stable bivalent and trivalent compounds, whereas nickel forms almost exclusively compounds in which it is bivalent.

Cobalt and nickel (and copper) differ from iron in their reactions with  $\text{NH}_4\text{OH}$  and with  $(\text{NH}_4)_2\text{CO}_3$ , for easily soluble ammonia compounds are formed, whereas in the case of iron an insoluble hydrous oxide is precipitated.

The most frequently encountered complex ions in which iron enters are  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Fe}(\text{CN})_6^{3-}$ , corresponding to which are  $\text{Co}(\text{CN})_6^{4-}$  and  $\text{Co}(\text{CN})_6^{3-}$ ; but cobalt forms in addition a very large number of complex ions, of which the most striking are those in which  $\text{NH}_3$  enters. All these complexes are of extreme importance, for it is not possible to detect directly iron or cobalt in them, nor to



obtain a reaction for  $\text{CN}^-$  in the complex by ordinary methods of procedure. Similar conditions obtain in other complex ions of iron and of cobalt.

As regards the relations of the secondary subgroup of Group I to Group VIII, little more need be added to the comments which have already been made.

Copper, like cobalt, forms a double thiocyanate with mercury. Silver falls in one of the horizontal short periods, and therefore has substantially nothing in common with the elements in the horizontal long periods.

Gold, in the third horizontal long period, is best grouped with osmium, iridium, and platinum, and like these elements enters into the formation of complex ions.

Since copper, silver, and gold fall in alternate horizontal short periods, these three elements have no microanalytical analogies and do not interfere with one another in the tests applied for their detection.

## DETECTION OF IRON

### A. By Means of Potassium Ferrocyanide — $\text{K}_4\text{Fe}(\text{CN})_6$ .

*Compounds Formed* —  $\text{Fe}_4(\text{Fe}(\text{CN})_6)_2$  or  
 $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ .

To the test drop acidified with  $\text{HCl}$  add a little powdered  $\text{K}_4\text{Fe}(\text{CN})_6$ . A dark blue precipitate or color indicates iron.  $\leftarrow$

Copper and uranium give dark brown ferrocyanides with  $\text{K}_4\text{Fe}(\text{CN})_6$ , and if present in high percentages may completely mask the reaction for iron by preventing the recognition of a blue coloration. Gallium gives a white gelatinous precipitate.

The reagent must be present always in considerable excess, for difficultly soluble ferrocyanides are formed with many other elements and there must be sufficient  $\text{Fe}(\text{CN})_6^{4-}$  ions to react with all precipitable cations. Most of these insoluble ferrocyanides are white or only faintly colored, but may so dilute the blue color of the iron compound as to cause it to be overlooked.

The test should be made at room temperature, for if the reagent is added to a hot, strongly acid test drop there may be sufficient decomposition of the  $\text{K}_4\text{Fe}(\text{CN})_6$  to give a blue color even in the absence of iron.<sup>1</sup>

The reaction is best performed upon material which has been evaporated to dryness with concentrated  $\text{HNO}_3$  in order to convert the iron into the ferric condition. Under these circumstances flocculent, dark

<sup>1</sup> Putnam, Roberts, and Selchow: *Am. Jour. Sci.* 15, 424 (1928).

blue, very insoluble ferric-ferrocyanide  $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$  is precipitated.

$\text{K}_4\text{Fe}(\text{CN})_6$  produces a dark blue precipitate with ferrous salts as well as with ferric, but under certain conditions the  $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$  may be peptized and a blue solution may result.

$\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$  is soluble in solutions of the fixed alkalis and is reprecipitated by  $\text{HCl}$ .

To obtain the best results, the  $\text{K}_4\text{Fe}(\text{CN})_6$  should be dried until anhydrous and finely powdered, and a small quantity of this reagent added to the test drop.<sup>2</sup>

A somewhat more convenient and sensitive reagent can be prepared by incorporating  $\text{K}_4\text{Fe}(\text{CN})_6$  in a fiber such as cotton or viscose-rayon.<sup>3</sup> The test drop should be of small diameter and the fiber when applied should have at least half its length outside the drop for the reason that the best reaction is obtained where a film has been drawn by capillarity around the fiber. The preparation is allowed to evaporate spontaneously to dryness and the fiber examined under the microscope.

The test for iron with potassium ferrocyanide fails in the presence of fluorides, phosphates, oxalates, citrates, tartrates, and organic hydroxy derivatives.<sup>4</sup>

#### Experiments.

(a) Test for Fe in simple salts

(b) Test in mixtures with other elements which will be precipitated by  $\text{K}_4\text{Fe}(\text{CN})_6$ .

(c) Test for iron in a ferrocyanide, by first decomposing the complex by ignition. Use Method B.

#### B. By Means of Potassium Thiocyanate — $\text{KSCN}$ .

*Compound Formed* —  $\text{Fe}(\text{SCN})_3$ .

The iron must be in the ferric condition. It is therefore best to treat the material with concentrated  $\text{HNO}_3$  and evaporate to dryness.  $\text{HCl}$  is added and the preparation is again evaporated to remove  $\text{HNO}_3$ . The residue is dissolved in water, acidified with  $\text{HCl}$ , and a relatively large fragment of  $\text{KSCN}$  is added. If iron is present, a pink or red coloration is produced; the intensity of the color varies with the amount of iron present.<sup>5</sup>

<sup>2</sup> Behrens: *op. cit.*, p. 26.

Behrens-Kley: *op. cit.*, p. 23.

<sup>3</sup> Mayrhofer: *Mikrochemie der Arzneimittel und Gifte*, p. 92.

<sup>4</sup> Feigl: *Zeit. anal. Chem.* 86, 1 (1931).

<sup>5</sup> If no color is visible in the test drop. Putnam, Roberts, and Selchow: *Amer. Jour. Sci.* 15, 261 (1928), suggest taking up the drop in a thin-walled capillary tube and examining it on a pure white background in a good light. Under the latter procedure a very faint pink can be more readily perceived.

Oxides of nitrogen must be absent; otherwise a red color may be obtained in the absence of iron.

$\text{HgCl}_2$  and a number of analogous salts discharge the red color; hence such interfering substances must be absent.

Molybdates in the presence of strong reducing agents give a red color with  $\text{KSCN}$ . This source of error is eliminated if oxidation with  $\text{HNO}_3$  has been followed as directed above.

$\text{KSCN}$  gives precipitates with salts of a number of elements. An excess of the reagent must therefore always be present if a satisfactory reaction for iron is to be obtained. When the precipitate of a white thiocyanate is a heavy one the intensity of the coloration of the  $\text{Fe}(\text{SCN})_3$  may be misjudged; in the face of such a condition, filter, or centrifuge, add more  $\text{KSCN}$ ; and, if the color is not distinct, examine by the capillary tube method.

The test may also be made by applying a viscose-rayon fiber which has been impregnated with  $\text{KSCN}$ , the application being made as outlined under the  $\text{K}_4\text{Fe}(\text{CN})_6$  method on page 268. When using  $\text{KSCN}$  fibers it is essential that the observations shall be made on the treated fiber outside the circumference of the drop. If more than mere traces of iron are present, the fiber will appear black.

If no well-marked reaction is obtained with  $\text{KSCN}$ , but a strong one with  $\text{K}_4\text{Fe}(\text{CN})_6$ , the iron is chiefly in the ferrous condition; but, if both reactions are well defined, it is not possible to determine whether ferrous compounds are present or absent. Under these conditions test with  $\text{K}_3\text{Fe}(\text{CN})_6$ .

The thiocyanate test for iron may fail in the presence of silver, lead, mercury, cadmium, zinc, fluorides, phosphates, oxalates, citrates, and tartrates.

### C. By Means of Quinoline and Ammonium Thiocyanate.

See page 194.

## DETECTION OF COBALT

### A. By Means of Potassium Mercuric Thiocyanate— $\text{K}_2\text{Hg}(\text{SCN})_4$ . *Compound Formed* — $\text{Co}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2$ .

The material is prepared for analysis by treatment with  $\text{HNO}_3$  as discussed under Zinc, page 136, and Copper, page 277.

Add the reagent by Method I or Method II, but better results are obtainable if Method III is used.

$\text{Co}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2$  separates in dark blue rectangular or tapering prisms, singly, or more often in many-armed radiates (Fig. 99, page 139). The reaction is specific though not very sensitive. The cobalt double thiocyanate is more soluble than those of zinc or copper and

will not separate at once, but appears after a few seconds. The influence of the presence of large amounts of zinc, cadmium, copper, and iron has been discussed at length under Zinc, page 136.

In the presence of much ammonium chloride or chlorides of the alkalis, the separation of the cobalt-mercury thiocyanate is materially retarded owing to its increased solubility. However, when a zinc salt is added to facilitate the detection of very small amounts of cobalt through the blue color given to the much less soluble, colorless, zinc-mercury thiocyanate, the addition of a little ammonium chloride tends to intensify the blue color.<sup>6</sup>

The cobalt-mercury thiocyanate salt often forms metastable solutions from which it is difficult to induce the separation of characteristic crystals.

Nickel in very concentrated solutions gives tiny spherulites or disks of very fine needles. A great excess of nickel may prevent the formation of the cobalt salt.

#### Experiment.

See Zinc. Method A, page 136.

#### B. By Means of Sodium Nitrite — $\text{NaNO}_2$ — and Cesium Nitrate — $\text{CsNO}_3$ .

*Compound Formed* —  $\text{Cs}_3\text{Co}(\text{NO}_2)_6 \cdot 1\frac{1}{2} \text{H}_2\text{O}$ .

To the neutral, very dilute test drop add a fragment of  $\text{NaNO}_2$ ; stir until dissolved. Add a little cesium nitrate. Warm and while still warm add a drop of acetic acid. Any  $\text{Co}^{++}$  present is converted into  $\text{Co}^{+++}$  and unites with  $\text{NO}_2^-$  to form the complex ion  $\text{Co}(\text{NO}_2)_6^-$ . The cesium salt of this complex ion is only very slightly soluble and immediately separates as a fine granular precipitate, yellow by reflected light, but usually almost black by transmitted light.

If precipitated in the cold it separates so finely dispersed as to appear to be amorphous, but from warm dilute solutions tiny cubes and octahedra can be obtained.

This salt can be considered as an analogue of  $\text{K}_3\text{Fe}(\text{CN})_6$ . The sodium cobaltinitrite is readily soluble. The corresponding nickel salt is too soluble to separate; hence a separation of cobalt from nickel may be thus accomplished; but the separation is not quantitative.

Calcium, strontium, barium and nickel are precipitated with the cobalt (Mayrhofer).

Theoretically the test should be very sensitive both for cobalt and for members of the potassium group, but since characteristic crystals are difficult to obtain.

<sup>6</sup> Cuvetier: *Zeit. anal. Chem.* 101, 108 (1935).

and metastable solutions prevail, the results are generally disappointing from the viewpoint of microscopical qualitative analysis.

In testing alloys and similar materials this test is of great value, especially since it can be extended to include the "triple nitrite reaction" by following the procedure given on page 209.

If a yellow precipitate is obtained with  $\text{KNO}_2$ , indicating the presence of cobalt, decant the supernatant liquid, wash the residue, add one or more drops of concentrated  $\text{HNO}_3$ , heat, and evaporate to dryness. Test the residue with  $\text{K}_2\text{Hg}(\text{SCN})_4$  as directed in Method A.

#### Experiment.

See Lead, Method C, page 207.

### C. By Means of Pyridine Hydrochloride and Ammonium Thiocyanate.<sup>7</sup>

*Compound Formed* —  $\text{Co}(\text{SCN})_2 \cdot (\text{C}_5\text{H}_5\text{N} \cdot \text{HSCN})_3$ .<sup>8</sup>

To the moderately concentrated test drop acidified with  $\text{HCl}$  add solid (or pasty) pyridine hydrochloride in an amount about the size of a pin head. Allow to stand a second or two; and, if no precipitate has been formed, add a large fragment of  $\text{NH}_4\text{SCN}$ .

Examine the preparation with the polarizer in place in order to take full advantage of the extraordinary pleochroism of the colored salts which may be formed. In the discussion which follows it is assumed that the preparation is illuminated with polarized light.

When cobalt is present, there is first formed around the thiocyanate fragments a blue zone and often blue oily droplets. In a few seconds long, thick, angular dendrites made up of rectangular tablets are formed. (See Figs. 166 and 167, page 251. In Fig. 166 the dendrites *R* are due to the reagent and are colorless, the dendrites *B* are a deep blue, whereas those marked *V* are a deep violet.) These crystals appear to belong to the monoclinic system; they exhibit strong pleochroism, the color change being from a light blue to a purple or violet. Pleochroism is best observed in the pinacoidal tablets that always accompany the dendritic aggregates. The rate of separation, habit, color, and hue of the crystals vary greatly with concentration conditions, and there is

<sup>7</sup> This is a modification of the test first described by Martini: *Mikrochemie* 7, 30 (1929). Pyridine, the base, is very volatile, has an intensely disagreeable odor and is moreover irritating and poisonous. These objectionable features are largely eliminated by employing pyridine hydrochloride, without materially affecting the usefulness of the test.

<sup>8</sup> This formula for the reaction product is suggested by Martini on the basis of the determination of crystallographic constants. The data obtained correspond to those given by Groth for a compound of this formula.

reason for the belief that the composition of crystals is also variable. It not infrequently happens that, instead of crystals, drops of a blue oily liquid are formed. Under these conditions the preparation should be allowed to stand until the test drop has passed to dryness through spontaneous evaporation. Colored metastable liquids are also formed with a number of different cations and with certain anions, but none of these droplets are blue save when cobalt is present. As the test drop passes to dryness, the metastable liquid crystallizes and blue or violet crystals can be readily distinguished in the mass of crystalline residue. The addition of a *very tiny* drop of water dissolves the residue, leaving the blue crystals of the cobalt pyridine thiocyanate, thus rendering them clearly visible. In a few seconds these blue crystals disappear and are replaced by blue oily droplets. When the test drop again passes to dryness, the blue metastable liquid crystallizes and the typical crystals of cobalt pyridine thiocyanate are formed.

Because of the tendency of the cobalt compound to form metastable oily drops which may not always be readily perceived in the mass of dendritic crystals, it is always best to allow the test drop to pass to dryness and search for blue crystals; these are to be found in segregated masses, usually near the circumference of the drop. Evaporation must not be hastened by heating, for the compound is easily decomposed.

The pyridine-metallo-compounds, formed when the test is performed as above indicated, are all soluble in absolute alcohol and can therefore be readily extracted from the dry residue. Hold the object slide in an almost vertical position with the corner carrying the test drop residue lowest. Allow a small drop of absolute alcohol to flow across the residue and collect at the corner of the slide. A second drop is applied and even a third if necessary. If now the corner of the slide carrying the drops of alcohol is touched to the corner of another clean slide which is also inclined, the alcoholic solution will flow onto the clean slide; or the alcohol may be decanted in the usual manner. Holding the slide well inclined during the spontaneous evaporation of the alcohol assures a concentration in a small volume and the deposition of crystals over a relatively small area.

Before performing tests with pyridine and ammonium thiocyanate the analyst should perform a "blank" test by adding to a drop of distilled water a tiny drop of HCl, then a relatively large mass of pyridine hydrochloride, and finally a large fragment of  $\text{NH}_4\text{SCN}$ . Note well the character of the crystals formed by the reagents alone. This "blank" is important since a few cations do not appear to influence the habit of the pyridine salt, while others materially modify it, but not sufficiently to permit identification of the modifying agent.

$\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{NH}_4^+$ , tartrates, oxalates, acetates, arsenates, arsenites, chromates, give no reaction and produce no noteworthy change in the crystals of the reagent.

The chlorides of  $\text{Ca}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Hg}^{++}$ ,  $\text{Al}^{+++}$ ,  $\text{In}^{+++}$ ,  $\text{Ti}^{+++}$ ,  $\text{Zr}^{+++}$ ,  $\text{Mn}^{++}$ ,  $\text{Ni}^{++}$  give colorless oily drops or a less dendritic form of the reagent but no crystals which can be used as specific tests.

Since the test is made in a solution acidified with  $\text{HCl}$ ,  $\text{Ag}^+$ ,  $\text{Tl}^+$ ,  $\text{Hg}^+$ ,  $\text{Pb}^{++}$ ,  $\text{WO}_3$ — ( $\text{Cu}^{+}[\text{?}]$ ;  $\text{Au}^{+}[\text{?}]$ ) may be precipitated when the  $\text{HCl}$  is added.

$\text{Fe}^{+++}$  gives a deep, blood-red or brownish-colored solution when the thiocyanate is added. If only a small amount of  $\text{Co}^{++}$  is present and much  $\text{Fe}^{+++}$ , the detection of  $\text{Co}^{++}$  is impossible; but, if the cobalt is in excess of the iron, blue crystals can be recognized, especially if the alcohol extraction is employed.

The formation of a precipitate when the pyridine hydrochloride is added to a concentrated solution of chlorides (before the addition of  $\text{NH}_4\text{SCN}$ ) indicates the presence of  $\text{Tl}^{+++}$ ,  $\text{Sn}^{++}$ ,  $\text{Sn}^{++++}$ ,  $\text{Ru}^{+++}$ ,  $\text{Pt}^{++++}$ ,  $\text{Ir}^{++++}$ ,  $\text{Pd}^{++++}$ , or  $\text{Au}^{+++}$ . But in dilute solutions no precipitate is formed with  $\text{Tl}^{+++}$ ,  $\text{Sn}^{++}$ , or  $\text{Sn}^{++++}$  until the  $\text{NH}_4\text{SCN}$  is added; then tablets or radiates of colorless acicular crystals appear at the circumference of the drop.

Rhodium and osmium give only a ring of yellow colloidal matter at the circumference of the drop as it goes to dryness.

$\text{Cu}^{++}$  forms two compounds: one, light yellow (Fig. 168, Y, page 251), in large elongated irregular plates or tablets or long somewhat acicular prisms; the other, brown or orange (Fig. 168, B, page 251), in long prisms, singly, in radiates or in irregular masses; these prisms are usually well formed with beveled or pyramidal ends. Both compounds are strongly pleochroic. Sometimes metastable oily drops are formed which do not crystallize until the test drop passes to dryness. Extraction of the residue with absolute alcohol is usually advisable. Copper does not interfere with the detection of cobalt. Uranyl salts and uranates on passing to dryness yield large, yellow, pleochroic prismatic crystals, singly and in radiates. The color and habit are different from those of the light yellow copper compound and there is little danger of mistaking copper for uranium, or *vice versa*, especially if the alcohol extraction is practiced.

Too much free mineral acid seriously interferes with all tests.

The sensitivity of this pyridine reaction for cobalt, copper, and molybdenum appears to vary greatly according to conditions and is quite low when applied to complicated mixtures. The compounds





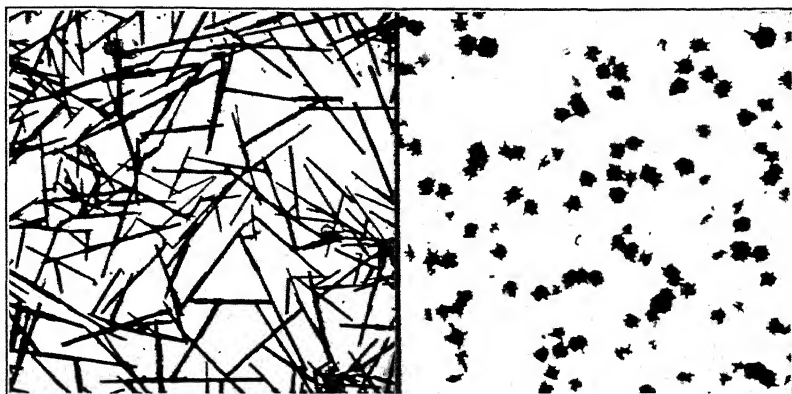


FIG. 170. Nickel with Dimethylglyoxime. 400 $\times$ .

FIG. 171. Ruthenium with Cesium Chloride. 400 $\times$ .

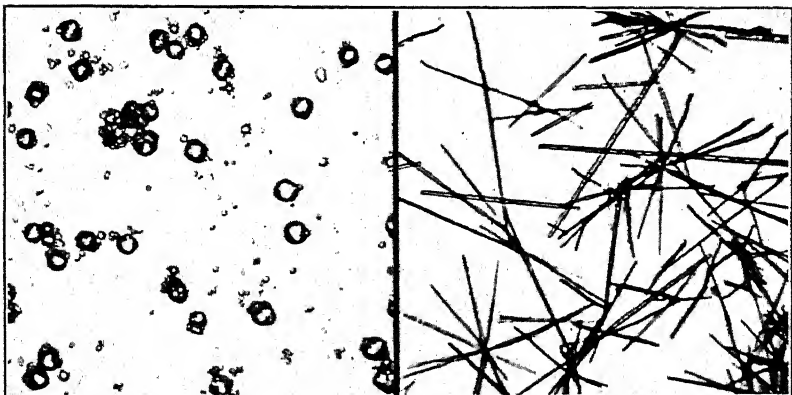


FIG. 172. Rhodium with Potassium Nitrite. 300 $\times$ .

FIG. 173. Palladium with Dimethylglyoxime. 150 $\times$ .

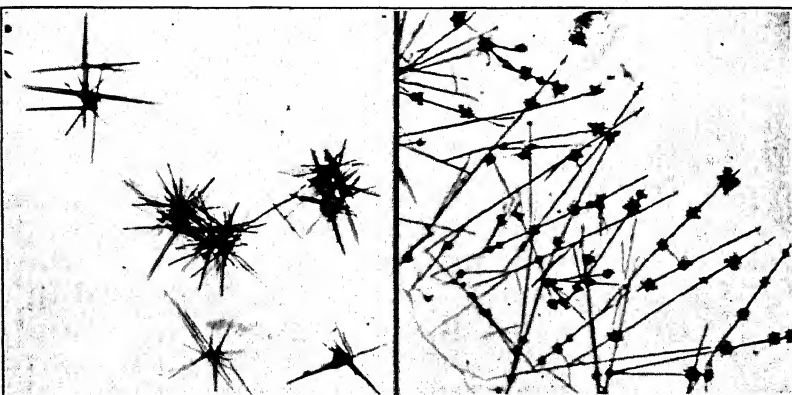


FIG. 174. Palladium with Cesium Chloride. 100 $\times$ .

FIG. 175. Palladium with Sodium Iodide and Ammonium Hydroxide. 200 $\times$ .

obtained as above. Cause the test drop to flow into the reagent. Warm gently.

Nickel yields immediately a rose-pink or magenta-colored precipitate, so finely divided at first as to appear to be amorphous. On standing a short time, fine, acicular, pink pleochroic crystals appear either in a felt-like mass or in irregular bristling clusters or in radiates of fine needles (Fig. 170, page 275). Sometimes relatively long, very slender, tapering prisms are obtained. Often a yellow precipitate is first formed, changing slowly into pink or red. The change is hastened by warming.

The pink, magenta, or reddish acicular crystals in alkaline solution are constant and peculiar to nickel; no other element reacts similarly. (See Palladium, page 293.)

The test is an exceptionally sensitive one even in the presence of an excess of other elements. Cyanides interfere, owing to the formation of a complex ion  $[\text{Ni}(\text{CN})_4]^{--}$ .

Neither cobalt nor copper gives a reaction with dimethylglyoxime, but if the cobalt or copper contains only "traces" of nickel a yellow precipitate is formed that does not readily change to pink on standing or on warming; even under these adverse conditions a careful study of the yellow compound will generally result in the discovery here and there of a few of the characteristic pink needles of the nickel salt. Only when cobalt or copper are in considerable excess do these elements interfere.

Copper can be removed by placing a weakly acidified drop upon a piece of sheet zinc; as soon as a black spot appears, the drop is decanted to a new position. When it is observed that the bright surface of the zinc is not stained at once, the drop is transferred to an object slide, strong  $\text{NH}_4\text{OH}$  is added, and the test for nickel is made as above. If sheet zinc or zinc foil is not available, zinc fragments can be used, removing them from the drop as soon as they blacken.

Cobalt can be separated by adding  $\text{KNO}_2$  (see page 270) to the acetic acid solution. Decant from the precipitated cobaltinitrite, add  $\text{NH}_4\text{OH}$  to the clear solution, and test with dimethylglyoxime.

When a sufficient volume of solution is at hand, the interference of cobalt may usually be eliminated by shaking the strongly ammoniacal solution with air, as recommended by Mayrhofer.<sup>9</sup>

Dimethylglyoxime gives with solutions of iron salts a red color. In testing for nickel, therefore, it is usual to obtain an indication of the presence of iron, especially if the material being analyzed contains ferrous compounds, for in the presence of ammonium salts the addition of  $\text{NH}_4\text{OH}$  to ferrous solutions will not completely precipitate a hydrous

<sup>9</sup> *Mikrochemie d. Arzneimittel u. Gifte* (Berlin, 1923), p. 117.

oxide, since double salts such as  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4$  or  $2 \text{NH}_4\text{Cl} \cdot \text{FeCl}_2$  are formed, and these double salts are relatively stable. If non-volatile organic acids are present,  $\text{NH}_4\text{OH}$  will not precipitate a hydrous ferric oxide, and ferric salts will be present in the ammoniacal solution to react with the dimethylglyoxime.

#### Experiments.

(a) Try the glyoxime reaction on salts of Ni in  $\text{NH}_4\text{OH}$  and in acid solution, and in different concentrations.

(b) Try the test upon Co compounds, and mixtures of Ni, Co, Cu, and Fe.

#### B. By Means of the Triple Nitrite Reaction.

*Compound Formed* —  $2 \text{KNO}_2 \cdot \text{Pb}(\text{NO}_2)_2 \cdot \text{Ni}(\text{NO}_2)_2$ .

To the neutral or ammoniacal solution sufficient acetic acid is added to make the test drop distinctly acid.  $\text{KNO}_2$  and  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  are then added as described under Lead, page 207.

When dealing with mixtures it is more convenient to start with the addition of  $\text{NaNO}_2$  and follow some such plan of procedure as is indicated on page 209, bearing in mind the warning given by Mayrhofer<sup>10</sup> that the alkaline earths and nickel are precipitated with the cobalt.

If copper is present in excess of nickel, the triple nitrite cubes will be colored dark brown or black and will mask the reaction for nickel. Copper can be removed by metallic zinc or iron, provided the reaction is not allowed to proceed too far. It is, however, inadvisable to depend upon the triple nitrite reaction for the identification of nickel, since it is not specific. Always have recourse to Method A.

### DETECTION OF COPPER

#### A. By Means of Potassium Mercuric Thiocyanate— $\text{K}_2\text{Hg}(\text{SCN})_4$ .

*Compound Formed* —  $\text{Cu}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2 \cdot \text{H}_2\text{O}$ .

The thiocyanate reaction for the detection of copper applies to bivalent copper, but not to monovalent copper compounds. Hence it may first be necessary to treat the material with concentrated  $\text{HNO}_3$ , evaporate to dryness, and dissolve the residue in water. The reaction is extraordinarily sensitive when the proper conditions are maintained.

The procedures, precautions to be observed, and sources of error have been discussed at length under Zinc, page 136.

It is particularly advantageous in the case of copper to make a preliminary test upon a rather highly concentrated test drop, allowing the preparation to stand for several minutes, and, after an examination of this preparation, deciding upon the proper dilution which will insure the formation of characteristic crystals.

When the percentage of copper is very low, the addition of a little

<sup>10</sup> *Op. cit.*, p. 118.

zinc acetate to the test drop (before the addition of the thiocyanate) will usually render the detection of the copper easier and surer, for the difficultly soluble zinc mercury thiocyanate is immediately precipitated and is colored lavender, brown, or even black, by traces of copper too small to be precipitated separately.

Small percentages of copper are generally completely masked by high percentages of cobalt or gold. Nickel may interfere when the test drop consists of a saturated solution of a nickel salt containing a trace of copper only. Dilution eliminates this source of error.

Materials very high in zinc, cadmium, or manganese, and low in copper, yield crystals faintly colored pinkish or lavender; as the percentage of copper increases, the depth of color also increases and finally becomes black, and simultaneously the yellowish-green dendrites of the salt  $\text{Cu}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2$  begin to appear.

Materials high in  $\text{Fe}^{+++}$  and low in  $\text{Cu}^{++}$  yield a double thiocyanate of copper, materially changed in habit and in color and almost masked by the intense red color of ferric thiocyanate. When iron is present, precipitate with  $\text{NH}_4\text{OH}$ , centrifuge or filter, and extract the precipitate repeatedly with strong  $\text{NH}_4\text{OH}$ . Unite the extracts, evaporate to dryness, take up with acid, and test with the thiocyanate reagent. In the presence of non-volatile organic acids the iron cannot be removed by this procedure. It is then necessary to ignite just sufficiently to destroy the organic matter, take up with  $\text{HNO}_3$ , evaporate to drive off the excess of acid, dissolve in water, and precipitate with  $\text{NH}_4\text{OH}$ .

Another method for the separation of the copper from iron is to place an acidified drop of the solution upon metallic zinc. The copper is precipitated upon the zinc whereas the iron remains in solution. The coating of copper can be scraped off or dissolved off and tested.

If manganese is present, add to the ammoniacal solution  $\text{H}_2\text{O}_2$  and heat to boiling; then proceed as suggested for the removal of iron. This treatment will also remove the cobalt.

In alloys high in lead and low in copper (*e.g.*, anti-friction alloys) the direct detection of copper is often unsatisfactory. It is best first to remove most of the lead by  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ . Alloys very high in silver and low in copper may also give trouble; remove the silver by precipitation with  $\text{HCl}$  before testing for copper.

### Experiments.

See Zinc, Method A, Experiments (b) and (d), page 144.

(a) Test for Cu in *very* dilute solution. Repeat, having a small amount of Zn present.

(b) Prepare a series of tests using varying proportions of Zn and Cu.

**B. By Means of the Triple Nitrite Reaction.**

*Compound Formed* —  $2 \text{KNO}_2 \cdot \text{Pb}(\text{NO}_2)_2 \cdot \text{Cu}(\text{NO}_2)_2$ .

This sensitive and characteristic reaction for copper has been described at length under Lead, page 207, Cobalt, page 270, and Nickel, page 277.

**Experiments.**

- (a) Test for Cu in  $\text{CuSO}_4$ ; in  $\text{Cu}(\text{NO}_3)_2$ , by the Triple Nitrite Reaction:
- (b) Try the reaction in acid solution; in ammoniacal solution.
- (c) Try in like manner a mixture of Cu and Ni, Cu and Co.

**C. By Means of Cesium Chloride —  $\text{CsCl}$ .**

*Compounds Formed* —  $2 \text{CsCl} \cdot \text{CuCl}_2$   
 $\text{CsCl} \cdot \text{CuCl}_2$ .

This reaction is discussed in detail under Tin, Method A, page 201; Antimony and Bismuth, Method A, pages 230–232 (Fig. 181, page 287).

**DETECTION OF SILVER****A. By Means of Hydrochloric Acid —  $\text{HCl}$ .**

*Compound Formed* —  $\text{AgCl}$ .

The test drop is strongly acidified with  $\text{HNO}_3$  and to it is added the reagent in excess by Method 1A, page 32.

$\text{AgCl}$  is precipitated at once as a heavy curdy mass without recognizable crystal form. The mother liquor is drawn off, the precipitate is washed with water acidified with  $\text{HNO}_3$ , and dissolved in  $\text{NH}_4\text{OH}$ . The ammoniacal solution is set aside, and upon spontaneous evaporation and loss of  $\text{NH}_3$  tiny cubes and octahedra of  $\text{AgCl}$  are formed from the decomposition of the compound  $\text{AgCl} \cdot 2 \text{NH}_3$  (Isambert). The crystals of  $\text{AgCl}$  are isotropic and have an extraordinarily high refractive index ( $n = 2.07$ ) and are therefore clearly visible though so small (Fig. 211, page 355).

Thorough washing of the precipitate before dissolving in  $\text{NH}_4\text{OH}$  is essential because there are many compounds that may seriously interfere with the formation of typical crystals; moreover the addition of  $\text{NH}_4\text{OH}$  to an improperly washed precipitate may cause the precipitation of hydrous oxides which may mask the reaction for silver.

$\text{AgCl}$  can also be recrystallized by boiling with concentrated  $\text{HCl}$ , but its solubility in this acid is so low that satisfactory crystals can seldom be obtained. Moreover the fumes arising from the hot acid are always annoying and may attack the metal parts of the microscope.

$\text{TiCl}_3$ ,  $\text{HgCl}_2$ , and  $\text{PbCl}_2$  are also precipitated by  $\text{HCl}$ . (See pages 156, 184, 206.)

In materials high in  $\text{Hg}^+$  and low in  $\text{Ag}^+$  the silver may escape detection because of the reaction of  $\text{NH}_4\text{OH}$  upon the  $\text{HgCl}_2$ . It has already been stated (page 156) that this reaction gives  $\text{HgCl}_2 \cdot \text{NH}_2$  plus metallic mercury. The finely divided mercury may under favorable conditions reduce the  $\text{AgCl}$  to metallic silver ( $\text{Hg}$  is more electropositive than  $\text{Ag}$ ) and thus there may be no  $\text{AgCl}$  left to be dissolved and recrystallized. On the other hand, Schoorl has shown that under certain conditions recrystallization of  $\text{AgCl}$  in the presence of  $\text{HgCl}_2$  gives rise to a complete change in the crystal habit of the  $\text{AgCl}$ , and that instead of cubes and octahedra, characteristic, highly refractive, moss-like dendrites in spherical masses are obtained.

Elements forming oxychlorides under exceptional conditions may be precipitated with the silver.

Precipitation of  $\text{AgCl}$  must always be made in relatively dilute solutions.

#### Experiments.

(a) Precipitate with dilute  $\text{HCl}$ , a test drop containing  $\text{AgNO}_3$ . Separate and wash the precipitate; then crystallize it, using  $\text{NH}_4\text{OH}$  as the solvent.

(b) In like manner test a mixture of  $\text{AgNO}_3$  and  $\text{HgNO}_3$ .

(c) Precipitate  $\text{AgCl}$ , wash, cover with a drop of water, and add a fragment of metallic zinc.

#### B. By Means of Ammonium Bichromate — $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ .

*Compound Formed* —  $\text{Ag}_2\text{Cr}_2\text{O}_7$  or  $\text{Ag}_2\text{CrO}_4$ .

To the test drop add sufficient dilute  $\text{HNO}_3$  to make it just distinctly acid. Add a fragment of the reagent to the center of the drop. Allow to stand undisturbed for a few seconds, then carefully transfer to the stage of the microscope.

$\text{Ag}_2\text{Cr}_2\text{O}_7$  [ $\text{Ag}_2\text{CrO}_4$ (?)] separates in dark red (blood-red or garnet-red) pleochroic plates. Thin plates may appear almost yellow and thick plates practically black. The crystals may be scale-like with irregular outlines, or may be rectangular, or elongated, unsymmetrical hexagons in outline. Five-sided plates are also formed. The plates occur singly and in irregular aggregates (Fig. 210, page 355).

Insufficiently acidified test drops, or those in which the concentrations are too high, yield tiny rods or slender acicular prisms so dark colored as to appear to be black. On standing, such preparations sometimes eventually also yield the more characteristic plates mentioned above.

$\text{Ag}_2\text{Cr}_2\text{O}_7$ (?) can be recrystallized from hot water, but this procedure

gives poor results. Far better preparations can be obtained by recrystallizing from hot  $\text{HNO}_3$  (1 : 4).

Silver bichromate is readily soluble in  $\text{NH}_4\text{OH}$ . On standing, dark red acicular crystals, skeleton forms, and dendrites separate. These crystals are believed to be complex salts containing one or more molecules of  $\text{NH}_3$ , probably  $\text{Ag}_2\text{CrO}_4 \cdot 4 \text{NH}_3$ .

The test drop should always be acidulated with  $\text{HNO}_3$ ; otherwise chromates of a number of other elements may be precipitated. (See pages 122, 161, 263.) When recrystallizing from  $\text{NH}_4\text{OH}$  the possible interference of these elements must be taken into account.

Normal orthorhombic  $\text{K}_2\text{CrO}_4$  added to neutral solutions of  $\text{AgNO}_3$  causes a precipitation of normal  $\text{Ag}_2\text{CrO}_4$ , but when the test drop is first acidified with  $\text{HNO}_3$  the crystals separating may be either  $\text{Ag}_2\text{CrO}_4$  or  $\text{Ag}_2\text{Cr}_2\text{O}_7$ , or a mixture, depending upon conditions of concentration and of acidity and upon the presence or absence of other ions. When recrystallized from hot  $\text{HNO}_3$  the salt separating usually consists of  $\text{Ag}_2\text{Cr}_2\text{O}_7$  alone.

In cold solutions lead is precipitated as heavy, bright yellow, pulverulent  $\text{PbCrO}_4$  without recognizable crystal form, but from hot solutions, thin, long, slender monoclinic prisms are obtainable. This salt is soluble in solutions of  $\text{NaOH}$  or  $\text{KOH}$ . If, however, only a minute quantity of alkali is brought into contact with the lead chromate, a bright red basic chromate is formed.<sup>11</sup>

When much lead is present, the bichromate reaction for the detection of silver may fail, for, instead of the dark red plates, small yellow prisms separate. In such an event, first remove most of the lead with dilute  $\text{H}_2\text{SO}_4$ , using a very dilute test drop. The test drop must be dilute with respect to silver, for otherwise  $\text{Ag}_2\text{SO}_4$  may be precipitated. When  $\text{H}_2\text{SO}_4$  is present, crystals of  $\text{Ag}_2\text{SO}_4$  separate with  $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_2\text{Cr}_2\text{O}_7$ . The crystals of  $\text{Ag}_2\text{SO}_4$  are then, however, not colorless but are pleochroic and yellow or brownish-red because of a solid solution of  $\text{Ag}_2\text{CrO}_4$  in  $\text{Ag}_2\text{SO}_4$ . Normal orthorhombic  $\text{Ag}_2\text{CrO}_4$  is isomorphous with  $\text{Ag}_2\text{SO}_4$ ,  $\text{Ag}_2\text{SeO}_4$ , and anhydrous  $\text{Na}_2\text{SO}_4$ .

Mercurous salts in  $\text{HNO}_3$  solution give a number of different compounds (see Mercury, page 161; Fig. 110, page 151), depending upon the conditions under which the test is made. These compounds differ sufficiently in habit from  $\text{Ag}_2\text{Cr}_2\text{O}_7$  to prevent confusing  $\text{Hg}^+$  and  $\text{Ag}^+$ , but if much  $\text{Hg}^+$  is present the dark red crosses and irregular bundles of prisms may completely mask the  $\text{Ag}_2\text{Cr}_2\text{O}_7$  crystals when the silver is present in very small amount only. Mercurous chromate is insoluble in alkalis, a distinction from lead. Bismuth salts yield irregular den-

<sup>11</sup> See Wagner *et al.*: *Zeit. anorg. allgem. Chem.* 208, 249 (1932).

ditric masses, small prisms, and hexagonal grains, which are orange or reddish-brown in color. The compound is probably bismuthyl bichromate  $(\text{BiO})_2\text{Cr}_2\text{O}_7$ . (?)

Dark red silver salts resembling the chromates are formed by arsenates. Vanadates form yellow or orange silver salts.

White alloys believed to contain silver can be tested for this element by drawing across a smooth surface a streak of a solution of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  in  $\text{HNO}_3$ . The color of the streak (in the absence of bismuth) is generally sufficient to indicate the presence or absence of silver. But if the streak is examined under the microscope by reflected light, there can be no doubt as to the presence or absence of silver, for the characteristic crystals of  $\text{Ag}_2\text{Cr}_2\text{O}_7$  can be readily perceived.

See under Chromium, Method A, page 244.

### Experiment.

#### C. By Means of Ortho-arsenic Acid or Ortho-arsenates — $\text{H}_3\text{AsO}_4$ . *Compound Formed* — $\text{Ag}_3\text{AsO}_4$ .

The reagent is applied by Method I, page 31, to the neutral or very slightly acid ( $\text{HNO}_3$ ) test drop, a gradient of acidity in the drop is desirable.

The best results are obtained when part of the  $\text{H}_3\text{AsO}_4$  in the reagent has been neutralized with  $\text{NH}_4\text{OH}$  but care must be observed that the acid is *never completely neutralized*.

Silver ortho-arsenate separates first as a fine, reddish, granular precipitate, rapidly changing to reddish brown with a tinge of violet, or changing into black crystallites, plates, and "prisms" of the cubic system. Imperfect rhombic dodecahedra are also formed. One of the characteristic features of this salt is the great variety of peculiar forms assumed by its crystals (Figs. 196, 197, page 337). Well-formed, well-developed crystals are seldom seen; the typical crystals are irregular dendrites, but aggregates bristling with fine parallel needles may develop on standing or on recrystallization from  $\text{NH}_4\text{OH}$ .

$\text{Ag}_3\text{AsO}_4$  is insoluble in acetic acid, moderately soluble in hot  $\text{HNO}_3$ , and readily soluble in  $\text{NH}_4\text{OH}$ . Recrystallization from  $\text{NH}_4\text{OH}$  gives characteristic crystals. In the absence of air the ammoniacal solution deposits colorless needles of the compound  $\text{Ag}_3\text{AsO}_4 \cdot 4 \text{NH}_3$  (Widman). This tetra-ammonia salt turns red when it comes in contact with the oxygen of the air, or when it loses  $\text{NH}_3$ .

Although the color and habit of  $\text{Ag}_3\text{AsO}_4$  are sufficiently characteristic to permit the easy recognition of silver in simple mixtures, the test cannot be considered as a dependable one since most of the metals



usually associated with silver are also precipitated by ortho-arsenic acid and may seriously interfere with or mask the reaction. However, the test has this in its favor that silver arsenate is the only known distinctly red arsenate.

#### Experiments.

- (a) Test a neutral solution of  $\text{AgNO}_3$  with  $\text{H}_3\text{AsO}_4$ , in the manner suggested above.
- (b) Recrystallize a preparation of  $\text{Ag}_3\text{AsO}_4$  from  $\text{HNO}_3$ .
- (c) Try recrystallizing another preparation with  $\text{NH}_4\text{OH}$ . Allow to stand after reprecipitation, and examine.
- (d) Test a mixture of Ag and Pb; then one of Ag and Hg.

### DETECTION OF THE PLATINUM GROUP

Ru, Rh, Pd; Os, Ir, Pt; Au

The rare elements of Group VIII, known also as the platinum metals, consist of gold (of Group I) and the two triad groups, ruthenium, rhodium, and palladium; and osmium, iridium, and platinum. In microscopical qualitative analyses of materials containing these elements the analyst finds himself confronted by almost insuperable difficulties. These difficulties are not so much a question of doubtful identity tests as of unsatisfactory separation methods when dealing with very small amounts of material. Moreover, these elements are not readily brought into solution.

Although the platinum metals are always found associated, can be separated only through complicated reactions, and have many properties in common, paradoxically, in no other triad groups do we find such widely divergent chemical properties.

Fortunately it is seldom that the analyst is required to make an analysis of material of absolutely unknown composition. The problem is usually to determine which of the platinum group are present in ores or alloys, or in salts. The salts, however, are seldom combinations of simple ions but are usually compounds in which the platinum metals are so combined with other elements as to form complex ions. In these complex ions the elements there combined seldom respond to their specific tests. Either the complex must first be destroyed or the analyst must be familiar with the chemical behavior of the rare metal complex ions which are likely to be encountered.

In recent years a remarkably large number of these complex ions have been found in which one or more members of the platinum group are components and the compounds into which they enter are extraordinarily intricate.

In the discussions of the tests as given in the following pages, the

authors assume that the material has finally been brought into solution by evaporation with aqua regia or through the action of chlorine gas, and that the excess of acid or chlorine has been removed. This treatment will give ruthenium, rhodium, and palladium as chlorides; iridium as chloroiridic acid; platinum as chloroplatinic acid; and gold as chloroauric acid. Osmium will probably have been driven off as the very volatile  $\text{OsO}_4$  or as chlorine compounds. Osmium therefore does not usually enter into the tests described for the other platinum metals, but must be sought by wholly different procedures; osmium may, however, remain in the aqua regia solution if the heating has not been at too high a temperature.

### DETECTION OF RUTHENIUM

#### A. By Means of Cesium Chloride — $\text{CsCl}$ .

*Compound Formed* —  $2 \text{CsCl} \cdot \text{RuCl}_3 (?)$

To the dilute test drop containing  $\text{RuCl}_3$ , acidified with  $\text{HCl}$ , the reagent is added by Method I or Method II.

A double chloride of cesium and ruthenium, of uncertain composition, is first precipitated as a barely visible turbidity; later exceedingly minute, highly refractive, spherical grains appear; these appear black by transmitted light but are faintly yellowish or brownish by reflected light. After standing some minutes, tiny dark brown disks are formed, many of them having a distinctly hexagonal outline; those near the circumference of the test drop gradually become drusy, and finally develop into tiny bristling radiates (Fig. 171, page 275). The sequence — tiny grains, disks, and radiates — appears to be specific for ruthenium.

Rhodium tested in the same way in dilute solution yields a precipitate whose refractive index is so near that of the solution that no details of structure can be resolved, but as the drop passes to dryness, anisotropic, cylindrical, oval, and lenticular crystals of a reddish-brown color appear; imperfectly developed prisms are also formed. Rhodium does not appear to interfere with the detection of ruthenium.

Palladium forms light brown, long, very slender acicular crystals, with ends tapering to a point, and are thus typical needles. The great majority of the crystals grow singly from the circumference into the drop. These needles also form curious irregular radiates that are specific for palladium (Fig. 174, page 275). Another characteristic feature of these radiates is the formation of queer, irregular, thin plates projecting from one side. The palladium salt is strongly birefringent and exhibits brilliant polarization colors. The extinction appears to be very slightly oblique. As the concentration rises, from spontaneous evapo-

ration, irregular aggregates of short, stout, tapering prisms are to be found.

Mixtures of ruthenium and palladium tested by Method II usually give at once, near the reagent fragment, masses of almost colorless typical trichites in long, curving, plume-like tufts, often extending completely across the field of the microscope. The individual filaments are so fine as to appear black. Near the circumference of the test drop disks of  $2\text{CsCl}\cdot\text{RuCl}_3(?)$  can be found, and later atypical needles of the palladium double salt appear. If a tiny drop of water is brought in contact with the trichiten crystals, they disappear at once and are replaced by the tapering acicular crystals of the palladium salt.

With platinum the same type-forms as of  $\text{K}_2\text{PtCl}_6$  are obtained, but always very much smaller. (See Potassium, page 65.)

In very dilute solutions containing iridium no separation of crystals occurs, and no indication of the salt  $\text{Cs}_2\text{IrCl}_6$  is obtained until evaporation has taken place. Concentrated solutions of iridium ( $\text{IrCl}_6$ )—yield yellow, rough spherical grains, irregular disks, rosettes, and lenticular crystals, singly or in aggregates. Under very favorable conditions octahedral crystals are obtained. The salt  $\text{Cs}_2\text{IrCl}_6$  is isomorphous with  $\text{K}_2\text{PtCl}_6$ . With rubidium chloride similar but larger crystals are formed (Fig. 187, page 295).

Both iridium and platinum unite with  $\text{NO}_2^-$  to form stable complex ions, the alkali salts of which are soluble.

### B. By Means of Thiourea — $\text{SC}(\text{NH}_2)_2$ . (Thiocarbamide.)

*Compound Formed* — Blue Color.<sup>12</sup> (Composition unknown.)

Thiourea appears to be one of the most useful reagents for differentiating between the members of the platinum group, for not only does it give characteristic crystalline precipitates or a color with each of them, but curiously enough, it is serviceable in mixtures if such mixtures are not too complex.

Thiourea forms colorless, strongly birefringent, orthorhombic bipyramidal crystals or thin glistening plates and tablets. If it contains ammonium thiocyanate as an impurity, the crystal habit is changed and long pearly needles or prisms are obtained. Thiourea forms addition products with metal salts and salts with anions. Its hydrochloride crystallizes in strongly birefringent prisms which exhibit parallel extinction and brilliant polarization colors.

The composition of the crystallizable reaction products obtainable

<sup>12</sup> Wöhler and Metz: *Zeit. anorg. Chem.* 138, 368 (1924).

with this reagent may vary depending upon the ratios of the salts present to the thiourea. Thus more than a single type of crystal with a given salt may appear in a test.

In the case of palladium, osmium, and platinum two different compounds appear to be formed, one in the zone where there is present an excess of the salt of the element, the other in the zone close to the reagent fragment where the solution contains an excess of the reagent. Although this complicates matters by introducing a large number of variables, it does not render the reactions impossible of interpretation, for the modified crystals formed are almost without exception characteristic of the mixtures.

The reaction with ruthenium takes place in strong HCl only.

Place near a corner of the object slide a large drop of concentrated HCl. To this drop add cautiously, a very little at a time, the concentrated chloride solution of the material to be tested until a yellowish or brownish tint is obtained. It is essential that the test drop thus prepared shall contain neither too little nor too much ruthenium and that the addition of the solution of the unknown shall not have materially diluted the HCl.

Add to the test drop several fragments of thiourea, a volume not less than this (o). Allow to stand for a short time; examine under the microscope. If crystals appear, note their habit. Warm the preparation and then hold it over a pure white background.

Ruthenium gives a beautiful, clear, blue color. The reaction is very sensitive and appears to be specific for ruthenium.

If the solution is too concentrated, the color produced is a greenish-blue and so intense as to be almost black (the green being the result of the yellow of the  $\text{RuCl}_3$  plus the blue of the compound formed by the thiourea).

Warming is essential for the development of the color, although at times, on standing at room temperature, a recognizable blue tint may appear.

Osmium as  $\text{OsO}_4$  in concentrated HCl gives instantly in the cold a deep carmine-red color and red crystals are formed. According to Tschugaeff<sup>13</sup> the red color is due to the formation of a complex having the formula  $\text{Os}(\text{NH}_2\cdot\text{CS}\cdot\text{NH}_2)_6\cdot\text{Cl}_3\cdot\text{H}_2\text{O}$ . These crystals usually take the shape of thin rectangular plates, of H's, X's, or may be envelope-like in appearance. The crystals are pleochroic, strongly birefringent, and exhibit brilliant polarization colors. The envelope-like crystals may grow into aggregates of thin irregular plates. Irregular radiates are commonly present (Fig. 178, page 287).

<sup>13</sup> *Compt. rend.* 167, 235 (1918).

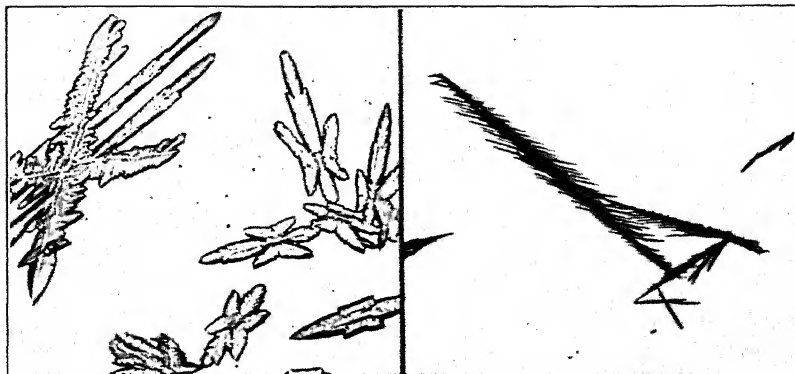


FIG. 176. Palladium with Thiourea.  
100 $\times$ .

FIG. 177. Platinum with Thiourea.  
100 $\times$ .

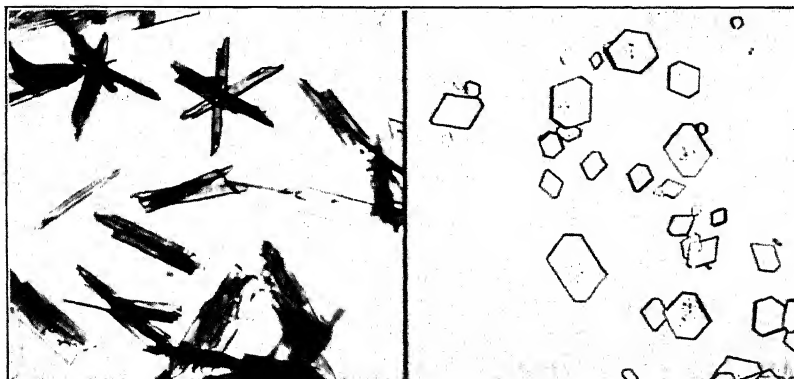


FIG. 178. Osmium with Thiourea.  
100 $\times$ .

FIG. 179. Gold with Thiourea.  
100 $\times$ .

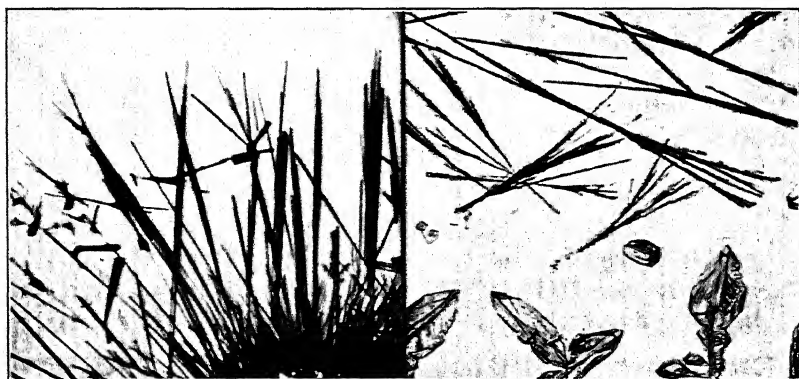


FIG. 180. Gold with Thallous  
Nitrate. 70 $\times$ .

FIG. 181. Copper with Cesium  
Chloride. 100 $\times$ .

In addition to the skeleton crystals there appear to be always formed many tiny crystalline aggregates that develop into thick stars, so deeply colored as to appear black. This compound is probably anisotropic, but the crystals are too thick and too deeply colored to permit accurate observations.

Preparations containing both ruthenium and osmium, when warmed, give varying shades of violet or purple according to the relative amounts of these two elements, *i.e.*, depending upon whether blue or red predominates. In mixtures the separation of the osmium crystals is retarded but not prevented. In mixtures of ruthenium and osmium, the crystals of the osmium compound are smaller and their tint slightly changed; but in all proportions both ruthenium and osmium can be detected simultaneously.

Rhodium gives first a very finely granular precipitate growing outward from the reagent fragment. When heated there is no appreciable change in color, but curious, small, reddish-brown botryoidal masses appear and the granular precipitate becomes flocculent. These peculiar crystal masses are formed only when the concentration of rhodium is relatively high. In dilute solutions none are to be found until the test drop has passed substantially to dryness.<sup>14</sup>

Mixtures of ruthenium and rhodium give the blue reaction for ruthenium unless the concentration of rhodium is very high, when a tinge of green is alone obtainable. But if the caution given above is followed and a test drop employed which is only just faintly yellow, an unequivocal reaction for ruthenium can always be obtained. When both ruthenium and rhodium are present in considerable amounts, there usually appear, after heating, deep blue-black disks, spheres, and botryoidal masses.

Test drops containing  $\text{H}_2\text{IrCl}_6$  are decolorized when thiourea is added. The decolorization proceeds more rapidly on warming. The original reddish solution eventually becomes water-white. No crystals separate. The presence of iridium appears to have little effect upon the color reaction for ruthenium. The only influence exerted appears to be a slight lowering of the sensitivity of the reaction, *i.e.*, the intensity of the blue is reduced but its hue is unchanged.

Palladium gives instantly, in the cold, a yellow or orange zone about the reagent fragments. Under the microscope the outer edge of the advancing zone is seen to consist of small orange-red or brown, moss-like, dendritic aggregates. In concentrated solutions this orange-red,

<sup>14</sup> According to Volkov: *Ann. Inst. Platine (U.S.S.R.)* 12, 79 (1935), the compound formed is  $[\text{Rh}(\text{SCN}_2\text{H}_4)_5]\text{Cl}_3$  or if the thiourea is in excess, two compounds are formed  $[\text{Rh}(\text{SCN}_2\text{H}_4)_5\text{Cl}]\text{Cl}_2$  and  $\text{Rh}(\text{SCN}_2\text{H}_4)_6\text{Cl}_3$ .

finely crystalline, difficultly soluble compound coats the reagent fragments and prevents the reagent from passing into solution.

Between the zone in which this difficultly soluble orange compound exists and the reagent fragments, a second very characteristic, bright yellow compound is formed. It separates in skeleton crystals in the shape of halberd heads (Fig. 176, page 287), rhomb-shaped plates or rhombs in which both acute angles are cut off perpendicular to the long axis of the rhombs. Radiates of slender prisms are also formed. All crystals are strongly birefringent, show brilliant polarization colors, and the prisms and plates give oblique extinction. The habit of the crystals formed with thiourea varies with concentrations of reagent and palladium.

Mixtures of palladium and ruthenium, when warmed, give the clear blue of ruthenium without destruction of the palladium crystals. But if ruthenium is greatly in excess of palladium, the halberd type of crystal is replaced by X's and short stout prisms.

Platinum (as  $\text{H}_2\text{PtCl}_6$ ) like palladium gives in the cold two different compounds, one yellow, one brown; usually the former exists for a short period only and is replaced by an abundance of long, reddish-brown, feathery dendrites (Fig. 177, page 287).

Mixtures of ruthenium and platinum, warmed, give the blue of ruthenium. In the cold the formation of typical crystals of platinum is not prevented. Heating dissolves them and they reappear on cooling.

Gold gives an orange-red precipitate in the cold, with a slight reduction to metallic gold, but in the zone immediately about the reagent, thin, practically colorless, hexagonal plates, singly and in foliated masses, are formed. They are weakly birefringent and exhibit blue and gray polarization colors. Heated they dissolve and reappear on cooling (Fig. 179, page 287).

Mixtures of ruthenium and gold give the blue color of ruthenium and the orange-red and colorless crystals of the gold compounds.

Many bivalent elements give a white granular or exceedingly fine crystalline precipitate with thiourea in the cold, but in all the cases we have tried there has been no prevention of the blue color of ruthenium, nor does there appear to be interference with the formation of the crystalline precipitates given by the platinum group of metals.

Cobalt salts give a blue color *at once, in the cold*; when added to concentrated  $\text{HCl}$  before the thiourea is added, the latter reagent causes no change.

The analyst will have little difficulty in interpreting the reactions obtained, if he will always use large fragments of the reagent, test drops at least twice as large as customary in other tests, and *never*

*neglect to perform the test on several different concentrations of the material in concentrated HCl. It is also essential that the preparations be allowed to stand for some time at room temperature.*

The following tabulation may serve as a guide in the interpretation of results, but it is obvious that it does not, and cannot, include all the combinations possible.

The preparation is allowed to stand at room temperature for a short time and then examined under the microscope.

### Thiourea as a Reagent

Red H's, X's, prismatic plates.....	Os
Thick brownish-red or black stars and aggregates.....	Os
Brown, reddish-brown, or black botryoidal grains.....	Rh
Brown dendrites, usually feathery.....	Pt
Dark-colored (brown?), moss-like groups of very tiny crystals.....	Pd
Yellow skeleton crystals, rhombs, elongated six-sided plates.....	Pd
Orange-red tiny dendrites.....	Au, Os
Colorless hexagonal plates in foliated masses.....	Au
Yellow radiates of acicular prisms and brown feathery dendrites.....	<div style="display: inline-block; vertical-align: middle;"> <div style="display: inline-block; vertical-align: middle;"> <div style="display: inline-block; vertical-align: middle;">Pd</div> <div style="display: inline-block; vertical-align: middle;">and</div> <div style="display: inline-block; vertical-align: middle;">Pt</div> </div> </div>
Brownish moss-like aggregates and brown feathery dendrites.....	<div style="display: inline-block; vertical-align: middle;"> <div style="display: inline-block; vertical-align: middle;">Pd</div> <div style="display: inline-block; vertical-align: middle;">and</div> <div style="display: inline-block; vertical-align: middle;">Pt</div> </div>
Very large radiating groups of feathery dendrites, either colorless or rose-pink (pleochroic).....	<div style="display: inline-block; vertical-align: middle;"> <div style="display: inline-block; vertical-align: middle;">Os</div> <div style="display: inline-block; vertical-align: middle;">and</div> <div style="display: inline-block; vertical-align: middle;">Pt</div> </div>

After warming, the preparation is held over a white background:

A clear blue color.....	Ru, (Co)
A red color and crystals.....	Os
A violet or purple color.....	Ru and Os

### DETECTION OF RHODIUM

#### A. By Means of Potassium Nitrite — $\text{KNO}_2$ .

*Compound Formed* —  $3\text{KNO}_2 \cdot \text{Rh}(\text{NO}_2)_3$ .

The reagent is applied by Method II, page 33, to a dilute test drop acidified with acetic acid.

In a few seconds a faintly yellow turbidity results, which slowly increases in amount, becomes distinctly granular in character, and finally develops into tiny, rough, rounded grains, singly, in strings of two or three, or grouped in irregular botryoidal masses (Fig. 172, page 275). These crystalline grains are isotropic. For their resolution a magnification of 150 to 200 $\times$  is usually essential.



When formed very slowly from dilute solutions, cubical and octahedral grains can be found, but these always have their edges and angles rounded.

If the test drop is highly concentrated with respect to rhodium, there will be formed about the fragment of  $\text{KNO}_2$  a reddish-brown zone, of a turbidity so dense that its resolution into distinct crystalline granules is impossible.

The addition of  $\text{CsCl}$  increases the sensitivity of the test to a certain degree, but little appears to be gained as regards the size of the crystals or the character of their development. In many cases the addition of  $\text{CsCl}$  is undesirable because of its marked tendency to form easily crystallizable double chlorides with other elements, and the separation of these double chlorides may completely mask the reaction for rhodium.

The nitrite reaction permits the detection of rhodium in the presence of ruthenium and palladium.

In dilute solutions ruthenium yields no precipitate, or at the most only a very slight turbidity of what appear to be tiny black grains which neither increase in numbers nor in size on standing. In very concentrated solutions a faint brown flocculent precipitate may be produced or tiny colorless(?) isotropic disks may appear; but these cannot be confused with the rhodium salt.

Palladium is not precipitated, but just before the drop passes to dryness through spontaneous evaporation there separate near the circumference of the drop long, narrow, irregularly tapering, bent prisms of a bright yellow color. Masses of trichiten crystals are also obtained, but no globulites.

In solutions containing  $\text{H}_2\text{IrCl}_6$  or  $\text{H}_2\text{PtCl}_6$  a precipitate of  $\text{K}_2\text{IrCl}_6$  or  $\text{K}_2\text{PtCl}_6$  is obtained, or, if the conditions are just right, a complex soluble iridonitrite or platinonitrite may be formed.

In test drops the iridium complex appears to be somewhat less soluble than that of the platinum complex, for in drops in which the concentration of iridium is high there may separate small drusy disks and spherulites or curving blades and rosettes.

Osmium gives no perceptible reaction with  $\text{KNO}_2$ .

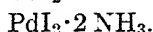
Cobalt forms a yellow, difficultly soluble, double nitrite that is indistinguishable from that of rhodium. (See Cobalt, page 270.)

If lead is present, nickel and copper will be precipitated also. (See Triple Nitrite Reaction, page 207.)

**B. By Means of Thiourea.**—See pages 285–290.

## DETECTION OF PALLADIUM

## A. By Means of Sodium Iodide — NaI.

*Compounds Formed* —  $\text{PdI}_2$ .

To a moderately dilute solution add the reagent by Method II.

The fragment of NaI is immediately covered with a dense, opaque black precipitate appearing somewhat granular in a zone about the black-coated reagent fragment, and the liquid immediately in contact with the reagent turns brown owing to the formation of a soluble double iodide;  $\text{PdI}_2$  is slightly soluble in excess of the reagent.

Apply a drop of  $\text{NH}_4\text{OH}$  (1 : 1) by Method I. There are formed almost at once very long, slender, hair-like, dark brown crystals, appearing jet black. These long straight hairs form a network resembling an irregular spider-web. Shortly after the separation of the slender prisms, tiny, irregular, bristling aggregates are formed, free and attached at intervals along the hairs like a string of rough beads. These tiny aggregates develop into crosses, stars, and lichen-like radiates, or into radiates of fine needles; there can be seen also curious acicular dendritic clumps (Fig. 175, page 275).

A test giving such a great variety of crystal forms is always unsatisfactory, since it is next to impossible to control conditions so as to obtain the particular type of crystal that is strictly characteristic of the ion sought. However, the very long, very slender, opaque crystals that first separate appear to be specific for palladium.

From somewhat concentrated solutions, with an amount of NaI insufficient to convert all the palladium into  $\text{PdI}_2$ , there will be formed around the circumference of the test drop brownish-yellow, straight and curving dendrites of the compound  $\text{PdCl}_2 \cdot 2 \text{NH}_3$ .

Ruthenium in dilute solutions gives no crystal formation, but in concentrated test drops there is produced a black cloud, and when  $\text{NH}_4\text{OH}$  is added there is an instantaneous formation of an opaque black mass.

Rhodium forms first a dark orange precipitate about the NaI fragments; then there appear in a zone about these fragments deep yellow or orange disks. These disks in turn disappear and are replaced by a few tiny, deep orange grains. The addition of  $\text{NH}_4\text{OH}$  produces an immediate precipitation of an orange-colored gel.

With  $\text{H}_2\text{PtCl}_6$  and  $\text{H}_2\text{IrCl}_6$ , NaI gives no crystals other than the separation of iodine as a dense black precipitate, which may be crystalline or granular according to concentrations, acidity, rate of decomposition of NaI, etc. If  $\text{NH}_4\text{OH}$  is added, there will be formed the yellow octahedra of  $(\text{NH}_4)_2\text{PtCl}_6$ , the red octahedra of  $(\text{NH}_4)_2\text{PtI}_6$ , and

mixtures of the two. With iridium the corresponding deeply colored  $(\text{NH}_4)_2\text{IrCl}_6$  and  $(\text{NH}_4)_2\text{IrI}_6$  will be obtained.

KI may be substituted for NaI with advantage except when platinum or iridium is present.

For the behavior of other elements with KI, see pages 159, 160.

**B. By Means of Dimethylglyoxime** —  $\text{CH}_3 - \text{C} = \text{NOH}$   
 $\text{CH}_3 - \overset{\text{I}}{\underset{|}{\text{C}}} = \text{NOH}$

*Compound Formed* —  $\text{Pd}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2$ .

The aqua regia solution of the material to be tested is evaporated to dryness to remove the excess of acids; to the residue one or two drops of water are added, and then a large drop (about half the size of the test drop) of concentrated HCl. Several small fragments of dimethylglyoxime are then fully submerged in the test drop, and the preparation set aside for a few minutes.

If palladium is present, the glyoxime fragments become covered with short, projecting, slender, yellow needles which appear to be brown or black under the microscope. These needles attain a considerable length, a few become detached from the reagent and form radiates or irregular aggregates, but the majority remain attached to the reagent fragments (Fig. 173, page 275).

When the test drop is of sufficient size to ensure standing for some time without evaporating to dryness, yellowish-brown, delicate, long, thin prisms with square ends are formed. These prisms usually occur singly, near the reagent, but not attached thereto; they are of unequal width throughout their length and can be seen to be crossed by many parallel lines at right angles to their length; examined between crossed nicols this peculiar structure is shown to be due to twinning.<sup>15</sup> These prismatic crystals exhibit polarization colors and extinguish parallel to their direction of elongation.

This reaction, especially the peculiar and characteristic twinning, appears to be specific for palladium, but it is essential that the reagent be added to a concentrated test drop strongly acidified with HCl.

According to Putnam, Roberts, and Selchow, who have made a comprehensive study of this test for palladium, there are no other elements that give a similar reaction under the conditions outlined, nor are there any interferences with the test under these conditions.

The addition of the reagent by Method I has not proved satisfactory in our hands; an immediate precipitate of short, very fine, lemon-yellow needles is produced in a thin cloud. Even on long standing

<sup>15</sup> Putnam, Roberts, and Selchow: *op. cit.*, p. 430.

these tiny crystals rarely develop into forms of such size and character as to constitute a reliable test.

It is sometimes stated that platinum and gold react with dimethylglyoxime. We have been unable to confirm this in the case of platinum as  $\text{H}_2\text{PtCl}_6$ , but with gold as  $\text{HAuCl}_4$ , on long standing, tiny, very faintly yellow, prismatic plates with oblique ends are obtained. These plates are strongly birefringent and exhibit oblique extinction, but do not develop into the long twinned crystals characteristic of the palladium compound.

**C. By Means of Thiourea —  $\text{SC}(\text{NH}_2)_2$ . — (See pages 285–290.)**

**D. By Means of Ammonium Thiocyanate and Thallous Nitrate.**  
*Compound Formed —  $2\text{TlSCN} \cdot \text{Pd}(\text{SCN})_2(?)$ .*

To the large test drop, which must be moderately concentrated with respect to palladium, add fragments of  $\text{NH}_4\text{SCN}$ , stirring until any brown precipitate at first produced has completely dissolved. Drop into the preparation several small crystals of  $\text{TlNO}_3$ . Heat to boiling. Allow to cool slowly; do not chill on metal.

A yellowish-brown crystalline precipitate results, growing into lenticular prisms usually united in three's or in more or less symmetrical crosses or in irregular radiating aggregates. These crystals are remarkable for their light-scattering powers and appear to be jet black by transmitted light.

If the preparation is chilled, great numbers of curious, tiny dendritic aggregates are obtained in forms resembling lichens or clumps of moss.

To solutions of ruthenium chloride the addition of  $\text{NH}_4\text{SCN}$  changes the yellow liquid first to brown, then to plum color or a reddish purple. After the addition of  $\text{TlNO}_3$  and boiling, a violet solution is obtained, from which separate violet or black, rough, three-armed or four-armed dendrites; later long, doubly tapering needles appear, singly and in loose radiates of few arms. These needles are difficultly soluble in hot water, are strongly birefringent, and show brilliant polarization colors, with an extinction very slightly oblique. The dendritic aggregates are, however, readily soluble in hot water, from which they separate on cooling, so black that only their angular outlines can be made out.

Rhodium gives a brown amorphous precipitate, insoluble in boiling water and showing no evidence of crystallization.

Platinum and iridium give minute isotropic octahedra.

This interesting reaction is of value as a confirmatory test only and is not applicable to routine qualitative analyses, especially when dealing with complex mixtures. If chlorides are present, some thallium will be precipitated as chloride.

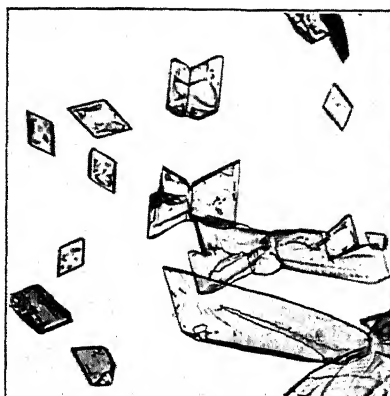


FIG. 182. Palladium with Aniline Hydrochloride. 100 $\times$ .

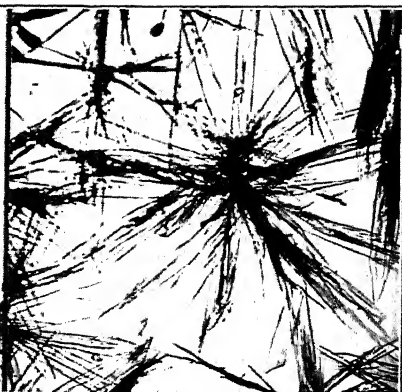


FIG. 183. Platinum with Aniline Hydrochloride. 50 $\times$ .



FIG. 184. Iridium with Aniline Hydrochloride. 200 $\times$ .



FIG. 185. Iridium with Aniline Hydrochloride. 70 $\times$ .

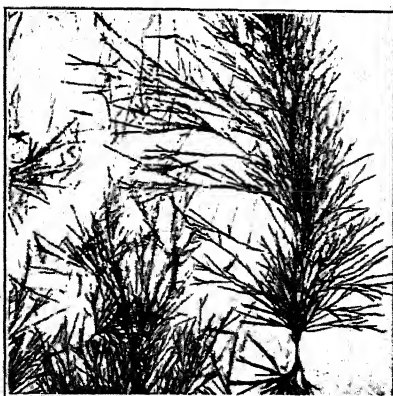


FIG. 186. Platinum Precipitated as Cupric Platinotetrammine Hydrochloride. 100 $\times$ .

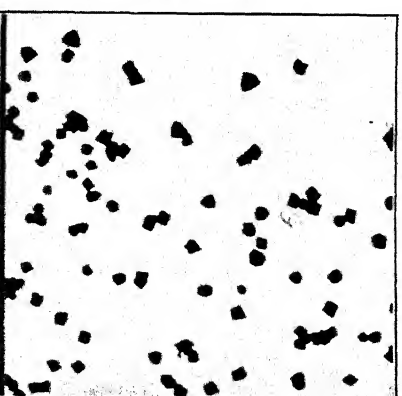


FIG. 187. Iridium with Rubidium Chloride. 200 $\times$ .

**E. By Means of Aniline Hydrochloride —  $C_6H_5 \cdot NH_2 \cdot HCl$ .**

*Compounds Formed* — Aniline salts with complex anions.

To the test drop strongly acidulated with HCl add a concentrated solution of the reagent by Method I, page 31.

Palladium yields curious polysynthetic prisms built up of thin plates, many groups of plates, or tablets resembling bow-knots, skeleton crystals, rhombiform plates, and irregular tablets. These very characteristic crystals are yellow, orange, or brown according to their thicknesses; they polarize brilliantly and are strongly dichroic, passing from yellow to brown. Extinction is oblique in the orientations commonly found upon object slides (Fig. 182, page 295).

Platinum gives very faintly yellow, thin, irregular plates and dendritic masses, wholly different in appearance from those formed by palladium and of an entirely different color (Fig. 183, page 295).

Iridium forms greenish X's and irregular skeleton and dendritic crystals, in appearance recalling  $PbCl_2$  when precipitated in the cold by HCl. Acicular, lath-shaped crystals and blades are also present as discrete crystals and radiates.

There is also formed a greenish-blue, amorphous precipitate resulting from the oxidation of the aniline (Figs. 184, 185, page 295).

Rhodium gives a yellow amorphous precipitate, and when the preparation passes to dryness a few small sheaves, radiates, and aggregates of dendritic crystals sometimes appear.

Ruthenium fails to react under the conditions of the test.

Osmium gives a colorless, crystalline crust around the circumference of the drop. No definite crystals are formed and no positive reaction is obtained.

Gold yields no crystals, but the aniline is oxidized by the  $HAuCl_4$  and a dense, flocculent, dark green precipitate results.

**Other Tests for Palladium.**

(a) With KCl added by Method II to an aqua regia solution there are obtained long, slender, yellow prisms with oblique ends. These prisms are strongly birefringent and exhibit brilliant polarization colors. Some give an extinction very slightly oblique to their direction of elongation; others appear to have parallel extinction. In solutions which are very strongly acid no crystals are at first formed, and the prisms appear after long standing only.

(b) With  $TiNO_3$  there is an instantaneous formation of a light brown, granular precipitate unless the solution is very dilute. If sufficiently dilute, curious, black, dendritic radiates are formed with arms ending

in disks; crosses and X's also abound. The latter appear to be skeletons of rectangular plates.

(c) With  $\text{NH}_4\text{OH}$  added by Method I to test drops strongly acidified with  $\text{HCl}$ , long, slender, rose-pink needles are formed in a felted mass. After standing a few minutes, one end of these needles begins to sprout and soon great feathery tassels are formed. If the solution is sufficiently concentrated with respect to palladium, some of the needles eventually broaden and become long, sharp-pointed prisms, which are strongly birefringent and show brilliant polarization colors. Their extinction is oblique, somewhat less than  $10^\circ$ . Ruthenium gives a black granular or flocculent precipitate, but no crystals. Rhodium gives a precipitate, similar, but reddish-brown in color.

(d) With oxalic acid and  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ . See Calcium, footnote, page 116.

### DETECTION OF OSMIUM

The microscopical detection of osmium is difficult and unsatisfactory save when dealing with a comparatively pure product such as "osmic acid" —  $\text{OsO}_4$ . The chief difficulty lies in the extraordinary volatility of the oxides and chlorides. If the material under examination is treated in the usual manner, it is probable that all of the osmium will be lost through volatilization, unless iridium is also present and the alloy "Osmiridium" is formed or present. It is therefore imperative that the attack by aqua regia shall be made in a distilling tube<sup>16</sup> of the types illustrated on page 19. The receiving end should be kept cool and should contain a strong solution of  $\text{KOH}$ . Behrens' suggestion that the condensate from the attack with aqua regia be received in a well-cooled tube and subsequently fractioned into  $\text{KOH}$  is a wise one, and the slightly increased time and labor involved are offset by the increased certainty of results.

Residues insoluble in aqua regia can be fused with  $\text{KOH}$  and  $\text{KClO}_3$  (1 : 1) in a tiny porcelain crucible and maintained at a low red heat until decomposition is complete. When thoroughly cool, the fused mass is moistened with water, a few drops of concentrated  $\text{HNO}_3$  added, and the crucible covered immediately with an object slide carrying a hanging drop of strong  $\text{KOH}$  (Behrens).

$\text{HNO}_3$  converts osmium into volatile  $\text{OsO}_4$ . Although osmium forms both  $\text{OsCl}_2$  and  $\text{OsCl}_4$ , the tetroxide  $\text{OsO}_4$  is the most stable compound of osmium; but even the osmates of potassium or sodium are relatively unstable, though their solutions permit of being concentrated at a gentle heat without loss of osmium.

Osmium is tested for by the addition of alcohol as below.

<sup>16</sup> See also Behrens-Kley, *op. cit.*, p. 250.

**A. By Means of Potassium Hydroxide and Alcohol.**

*Compound Formed* —  $\text{K}_2\text{OsO}_4 \cdot 2 \text{H}_2\text{O}$ .

If the material to be tested is a water-soluble crystalline compound, dissolve it in a drop of a strong solution of KOH placed at the corner of a slide. Osmium will give in KOH a yellow or brown solution. Test the reaction by touching the drop with a "litmus-silk" fiber. The drop must be strongly alkaline.

Tip the slide at an angle of about  $30^\circ$  so that the test drop is at the lowest point, add a tiny drop of absolute alcohol about 2 mm. above the test drop, and allow it to flow into the test drop. If the slide is not tipped, the alcohol and test drop mixing will flow over the slide. In a few seconds add another drop of alcohol. As soon as all action has ceased, examine the preparation under the microscope, first holding it over a white background to observe the color.

Potassium osmate,  $\text{K}_2\text{OsO}_4 \cdot 2 \text{H}_2\text{O}$ , separates in well-developed, clear-cut, violet, highly refractive orthorhombic "octahedra" which are strongly birefringent and exhibit brilliant polarization colors. Many of the octahedra show pinacoidal faces, and many develop into elongated forms. This salt is readily soluble in hot water and can be recrystallized repeatedly. Occasional preparations are obtained in which all the crystals first formed are elongated pseudo-octahedra (Figs. 188, 189).

When the material to be tested consists of a condensate which has been absorbed in KOH, a drop is placed at the corner of a slide and the alcohol applied as above.

**B. By Means of Thiourea —  $\text{SC}(\text{NH})_2$ . — (See pages 285–290.)****C. Other Tests for Osmium.**

(a) Probably the most sensitive and characteristic test is the odor of the vapor of osmium tetroxide, which cannot be mistaken. It is violently irritating and attacks the mucous membranes; hence great care must be exercised when handling even minute amounts of compounds of osmium.

(b) Osmium compounds are easily reduced to the metal by most organic compounds. Hence care must be taken to exclude such materials when testing for osmium. This ease of reduction is the basis for the use of "osmic acid" in testing for fats and oils, with which it gives a black color.

(c) Osmic acid dissolved in a little strong HCl gives with CsCl yellowish isotropic octahedra and plates of a double chloride of uncertain composition. A relatively high concentration of osmium is



required, and the absence of too much water. The test appears to be of no value in routine testing, for in our experience it is uncertain and

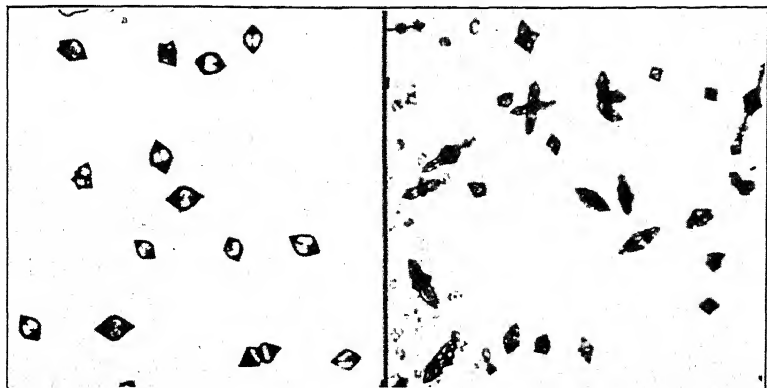


FIG. 188. Osmium Precipitated as Potassium Osmate. 100X.

FIG. 189. Osmium Precipitated as Potassium Osmate. 200X.

unreliable. Test drops which fail to yield a precipitate cannot be concentrated by heating because of the volatility of  $\text{OsO}_4$ .

(d) In acid solution osmium is precipitated, black, by metallic zinc,  $\text{FeSO}_4$ ,  $\text{SnCl}_2$ , and many other reducing agents.

## DETECTION OF IRIDIUM AND PLATINUM

In the absence of osmium, alloys of both these elements are soluble in aqua regia. Both yield complex anions with halogens, the potassium-group salts of which are characteristic and easily obtained.

It is assumed in this discussion that the material has been repeatedly evaporated with aqua regia. Under these conditions the solution to be tested will be a  $\text{HCl}$  solution of  $\text{H}_2\text{IrCl}_6$  or  $\text{H}_2\text{PtCl}_6$  or a mixture, and any  $\text{IrCl}_4$  or  $\text{PtCl}_4$  first formed will have been converted into chloro-acids.

To the moderately dilute test drop add  $\text{KCl}$  by Method I.  $\text{K}_2\text{PtCl}_6$  separates in isotropic orange-yellow octahedra (see Potassium, page 65);  $\text{K}_2\text{IrCl}_6$  in tiny, dark red isotropic octahedra. These two salts form isomorphous mixtures of intermediate color. A similar salt is formed with  $\text{RbCl}$  (Fig. 187, page 295). For differentiating between iridium and platinum the reaction with  $\text{RbCl}$  is superior to that with  $\text{KCl}$ , for not only is the rubidium salt more readily formed but is darker red than the potassium chloroiridate; the color is so intense in fact as to appear black by transmitted light.

It has already been pointed out that the solubilities of the alkali salts of  $\text{H}_2\text{PtCl}_6$  decrease with a rise in the atomic weight of the alkali, *i.e.*, K,  $(\text{NH}_4)$ , Rb, Cs,  $(\text{TI}^+)$ . The sensitivity of the reaction for platinum is therefore increased by substituting for potassium any one of this series; but the size of the crystals formed is also greatly diminished, so that with thallium only a fine granular precipitate is obtained but the sensitivity is increased over a hundredfold (Behrens).

Platinum is differentiated from iridium by the difference in the color of the salts, and by the fact that  $(\text{NH}_4)_2\text{IrCl}_6$  is much more soluble than  $(\text{NH}_4)_2\text{PtCl}_6$  and forms a reddish solution instead of a yellow precipitate. Furthermore, whereas very dilute solutions containing platinum as  $\text{H}_2\text{PtCl}_6$  give an instantaneous precipitate with  $\text{TiNO}_3$  consisting of tiny yellowish octahedra, solutions containing  $\text{H}_2\text{IrCl}_6$  are reduced by the thallium salt and yield a blackish-green flocculent precipitate but no crystals.

Palladium as  $\text{H}_2\text{PdCl}_6$  gives  $\text{K}_2\text{PdCl}_6$  in red octahedra;  $\text{K}_2\text{PtCl}_6$  precipitated in the presence of palladium retains its octahedral form, and the crystals instead of being yellow are brown. Boiling a dilute solution before the addition of the alkali chloride will generally cause decomposition and reduction and precipitation of the palladium chloride. A similar treatment is without effect upon  $\text{H}_2\text{PtCl}_6$ . Pd as  $\text{H}_2\text{PdCl}_4$  yields brown prisms  $\text{K}_2\text{PdCl}_4$ .

Platinum may be differentiated from iridium and palladium by conversion into a cupric salt of platino-tetrammine chloride  $(\text{Pt}(\text{NH}_3)_4)\text{Cl}_2 \cdot \text{CuCl}_2$  or  $\text{Pt}(\text{NH}_3)_4 \cdot \text{CuCl}_4$ .<sup>17</sup>

The  $\text{H}_2\text{PtCl}_6$  must first be reduced by  $\text{SnCl}_2$ . This can be accomplished by dissolving metallic tin in  $\text{HCl}$  and adding tiny drops to the test drop until its yellow color has completely changed to brown; a slight excess of  $\text{SnCl}_2$  is not objectionable. Add a few fragments of  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ ; stir until dissolved, warming gently if necessary. Cool and add an equal quantity of  $\text{NH}_4\text{Cl}$ . If the reduction has been complete, no yellow octahedra should be precipitated. Now apply strong  $\text{NH}_4\text{OH}$  (1 : 1) by Method I. Hold the preparation over white paper. A blue-violet precipitate will be seen to have been produced. Under the microscope it will be found to consist of a great mass of slender needles, one end of which develops into feathery tufts like the tassels of maize or sugar-cane. On standing there may form, at the circumference of the drop, long, thin prisms with square or oblique ends singly or in tufts or radiates. This reaction is specific for platinum (Fig. 186, page 295), but unfortunately is neither very sensitive nor readily obtained, since the relative concentrations require careful adjusting. If

<sup>17</sup> Werner. See Urbain: *Chimie des Complexes* (Hermann, Paris), pp. 225, 234.

the stannous chloride contains an excess of acid the proportion of copper acetate must be high and that of ammonium chloride low.

If a palladium salt is substituted for the copper salt, similar crystals are obtained but they are brownish. In mixtures containing both copper and palladium, the blue-violet becomes a dirty violet. Chlorides or other divalent elements can take the place of copper or palladium, but the reactions obtained are not so readily interpreted.

In test drops rather high in platinum the reduction can be brought about by adding metallic tin. Part of the platinum is deposited upon the tin as a dark-colored coating, part is reduced to platinous chloride, for  $\text{SnCl}_2$  does not completely reduce  $\text{H}_2\text{PtCl}_6$  to metallic platinum.

It is obvious that the formation of this copper salt of platino-tetrammine is a means of distinguishing between platinous and platinic salts, or, to put it more correctly, between chloroplatinic acid and platinum chlorides.

Iridium gives no precipitate and no color with thiourea, but in the case of platinum the crystals formed are very characteristic and the reaction is a sensitive one. (See pages 285-290.)

**Separation and Identification of the Platinum Group in Alloys (and Minerals).**<sup>18</sup> — The finely divided material is extracted repeatedly with hot concentrated  $\text{HCl}$  to remove iron and other easily soluble metals.

The residue is repeatedly treated at room temperature with slightly diluted aqua regia as long as a yellow solution is obtained. The solution is tested for gold.

The residue insoluble in cold aqua regia is boiled with concentrated  $\text{HCl}$ , 6 part, concentrated  $\text{HNO}_3$ , 1 part, as long as anything dissolves. Solution: platinum, iridium, rhodium, palladium, members of the copper group, and perhaps gold. The residue will contain any ruthenium, iridium or osmium. (If iridium is absent, osmium will have been driven off.) If iridium is present, test the residue as directed under Osmium, page 297 (and also make a special distillation for osmium).

The solution containing platinum, iridium, rhodium, or palladium, etc., is evaporated almost to dryness and dissolved in water.

Precipitate the platinum and iridium with  $\text{NH}_4\text{Cl}$ . Add alcohol, filter or centrifuge, wash with alcohol the insoluble residue consisting of  $(\text{NH}_4)_2\text{IrCl}_6$  and  $(\text{NH}_4)_2\text{PtCl}_6$ .

Acidify with aqua regia and concentrate the united filtrates until

<sup>18</sup> This outline follows in the main the procedure of Behrens, with modifications of Noyes and Bray.

crystals begin to form. Test a large drop by means of  $\text{NH}_4\text{OH}$ , page 300. If both rhodium and palladium are present, the double chloride of rhodium and pallado-tetrammine will be obtained. Usually crystals of the chloride of pallado-diammine separate first, followed by those of the palladium-rhodium compound.

Iridium and rhodium can be separated from the copper group by treating with  $\text{NaNO}_2$  in acetic acid solution, warming, and adding  $\text{NaOH}$ . Iridium and rhodium form soluble nitrites, but the copper group is precipitated. Filter, add  $\text{HNaCO}_3$  to precipitate any lead present. Filter. Evaporate the filtrate with  $\text{HCl}$ , dissolve in water, and add  $\text{Na}_2\text{CO}_3$  and bromine, and filter off the precipitated iridium and rhodium oxides. Filter, wash, and test after solution in aqua regia.

The residue from the concentrated aqua regia, consisting of ruthenium and "Osmiridium," is fused with  $\text{KOH}$  and  $\text{KClO}_3$  and tested for osmium as on page 297, and for ruthenium as on page 284.

An alternative separation is that of Noyes and Bray:

The material is brought into solution by heating with concentrated  $\text{HBr}$ ; bromine is added from time to time until the reaction is complete. The solution is concentrated and transferred to a suitable distilling tube, a little water and  $\text{HNO}_3$  (16 *N*) added. Distil slowly until bromine vapors are no longer seen, collecting the distillate in  $\text{KOH}$  kept cold with ice water. Add  $\text{Na}_2\text{O}_2$  to the distillate until it is colorless, and continue the distillation. Osmium passes over as  $\text{OsO}_4$  and is fixed by the alkali. Set the distillate aside, and place a fresh solution of alkali to receive a distillate. Add to the contents of the distilling tube an equal volume of  $\text{HClO}_4$  (9 *N*) and continue the distillation. Ruthenium passes over as  $\text{RuO}_4$ .

Test the first distillate by adding alcohol. (See page 298.) (If osmium has passed over, the distillate will be yellow or brown.)

To a portion of the second distillate (orange or red) add alcohol; black metallic ruthenium is precipitated. To another portion add  $\text{HCl}$ ; a hydrous oxide is precipitated; centrifuge or filter and dissolve in aqua regia. Evaporate and test with thiourea. (See page 285.)

For the remaining elements rhodium, palladium, iridium, platinum, and gold dissolve the material in aqua regia; concentrate. Extract the  $\text{HAuCl}_4$  with ethyl acetate.

To the aqueous liquid add  $\text{HCl}$ , evaporate almost to dryness, take up with water, add  $\text{NH}_4\text{Cl}$ , and filter off the precipitate of  $(\text{NH}_4)_2\text{PtCl}_6$  and  $(\text{NH}_4)_2\text{IrCl}_6$ . The filtrate contains palladium and rhodium (and iridium, the latter in traces).

Evaporate the ethyl acetate, ignite the residue, dissolve in aqua regia, and test for gold. (See page 304.)

Dissolve the  $\text{NH}_4\text{Cl}$  precipitate in aqua regia, concentrate and test for platinum and iridium. (See pages 299–301.)

Evaporate the filtrate containing palladium and rhodium, boil with aqua regia, concentrate, and test for palladium (see page 292) and for rhodium. (See page 290.)

None of the above separations are quantitatively exact, but are usually sufficiently sharp to permit identifications save when only a "trace" of a given element is present.

In general it may be said that separations are seldom necessary if judgment is used in the selection of direct tests upon the material in question.

One of the latest and most comprehensive schemes for the separation of the metals of the platinum group is given below. According to its author, the separations are quantitative. It is based upon the separation of platinum from the other members of the group by means of an alcoholic solution of  $\alpha$  furildioxime.<sup>19</sup> Aside from difficulties in handling alcoholic solutions in microscopical qualitative analysis the scheme is an excellent one and will be found dependable.

**Scheme for the Qualitative Analysis of the Platinum Metals.**<sup>20</sup> — To a solution of the chlorides in dilute  $\text{HCl}$  (1 : 12) add a *very* slight excess of a one per cent alcoholic (95%) solution of dimethylglyoxime. Decant, filter or centrifuge. — Filtrate I. Precipitate *a*.

Precipitate *a*. Pd (See page 292.) Ignite, dissolve in aqua regia, evaporate. Test with thiourea. (See page 285.)

Filtrate I. Pt; Rh; Ru; Ir; Os Add a slight excess of a two per cent alcoholic solution of  $\alpha$  furildioxime, then a little alcohol ( $\frac{1}{10}$  total volume). Filter or centrifuge. Filtrate II. Precipitate *b*.

Precipitate *b*. Pt (See page 299.) Ignite. Dissolve in aqua regia and test with  $\text{KCl}$ . (See page 300.)

Filtrate II. Rh; Ru, Ir, Os Evaporate almost to dryness. Add  $\text{HCl}$  and  $\text{NaClO}_3$  to destroy the oximes. Add alcoholic  $\text{KNO}_3$ , avoiding an excess. Allow to stand a long time. Centrifuge. Filtrate III. Precipitate *c*.

<sup>19</sup> See Soule: *Jour. Amer. Chem. Soc.* 47, 981 (1925).

<sup>20</sup> Based upon Method of Ogburn: *Jour. Amer. Chem. Soc.* 48, 2493, 2507 (1926); *Jour. Chem. Education* 5, 1383 (1928).

Precipitate <i>c.</i>	Rh	(See page 290.)
Filtrate III.	Ru; Ir; Os	Boil until all oxides of N cease to be evolved and all alcohol has been expelled. Acidify with HCl. Evaporate almost to dryness. Add alcoholic NaOH. Boil. Centrifuge. Filtrate IV. Precipitate <i>d.</i>
Precipitate <i>d.</i>	Ru	As $\text{Ru}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$ . (See page 284.)
Filtrate IV.	Ir; Os	Evaporate to expel all alcohol. Acidify with dilute HCl. Add metallic zinc. When all reaction has ceased, filter or centrifuge. Filtrate V. Precipitate <i>e.</i>
Precipitate <i>e.</i>	Ir, Os	As metallic Ir, and metallic Os. Treat with a solution of freshly prepared NaOCl. Filter or centrifuge. Filtrate V. Precipitate <i>f.</i>
Precipitate <i>f.</i>	Ir	Dissolve in aqua regia. Test with KCl (see page 299); and with aniline hydrochloride. (See page 296.)
Filtrate V.	Os	Acidify with HCl. Add metallic zinc. Metallic Os is precipitated. Dissolve in aqua regia. Test with thiourea (page 285), or precipitate as potassium osmate (page 298).

### DETECTION OF GOLD

The material to be tested will probably have been brought into solution by means of aqua regia; hence it is assumed in the following tests that gold is present as chloroauric acid,  $\text{HAuCl}_4$ . On heating, this compound may be reduced to  $\text{AuCl}$ , a white salt insoluble in water, or, if heated still further, metallic gold is obtained. Hence care must be exercised when it is necessary to expel an excess of aqua regia.

#### A. By Means of Pyridine Hydrobromide — $\text{C}_5\text{H}_5\text{N} \cdot \text{HBr}$ — and Hydrobromic Acid — $\text{HBr}$ .

*Compound Formed* —  $\text{C}_5\text{H}_5\text{N} \cdot \text{HBr} \cdot \text{AuBr}_3$ .<sup>21</sup>

*Reagent:* Pyridine, 1 volume; 40 per cent Hydrobromic Acid, 9 Volumes.

The aqua regia solution of the material to be tested for gold is carefully evaporated to dryness. The dry residue is dissolved in water.

<sup>21</sup> Putnam, Selchow, and Roberts: *Amer. Jour. Sci.* 15, 455 (1928).

To a concentrated test drop, a drop of the reagent is added by Method I, page 31.

Gold yields yellow, orange, and dull red, thin, elongated almost rectangular plates and prisms, exhibiting an oblique extinction of about  $10^\circ$  and remarkably strong pleochroism—orange or brownish when the crystals lie with their directions of elongation at right angles to the plane of a nicol and colorless or pale yellow when parallel to the plane of vibration of a nicol, Fig. 157, page 235.

With dilute test drops the reaction is less satisfactory for the reason that imperfectly developed crystals and dendritic clumps are obtained.

It is essential that the reagent be prepared as designated and that there shall be present in the treated test drop an excess of hydrobromic acid.

This pyridine-hydrobromic acid reaction for gold is one of the very rare examples of a "crystal reaction" in which no interferences have as yet been reported.

Lead yields with the reagent colorless, acicular, non-pleochroic crystals. If the residue from the aqua regia solution of the unknown was cold when extracted with cold water and the reagent was applied cold, the likelihood of there remaining in solution sufficient lead to mask the reaction for gold is very remote. If in doubt, add a little NaBr to the test drop before applying the reagent.

#### **B. By Means of Potassium Mercuric Thiocyanate— $K_2Hg(SCN)_4$ . *Compounds Formed (?)*.**

To a moderately dilute test drop acidulated with  $HNO_3$  and containing the gold as Chloroauric Acid, add the reagent by Method II, page 33.

The most satisfactory reaction is obtained when the reagent is introduced in a single firm fragment which will dissolve slowly. If gold is present, the fragment will be covered at once with a reddish or pinkish orange precipitate consisting of minute acicular crystals. Examine between crossed nicols and note their distinctly red color (see Copper, page 277).

Any excess of acid in the original material should be removed by evaporation before taking a portion for a test drop. Buffering with sodium or ammonium acetate leads to the removal of the nitric acid and the precipitation of a white amorphous aurous compound and no auric salts will be found. In all tests some aurous salts separate; sometimes the reduction proceeds far enough to yield even a little metallic gold.

After standing a few seconds, yellow mossy dendritic masses appear which bear a striking resemblance to those obtained with copper; compare Figs. 100 and 101, page 139.

When copper is present, the typical reactions for both copper and gold are obtained; the two compounds do not appear to be isomorphous. The same is true of mixtures of cobalt and gold.

In the case of nickel, however, the gold dendrites are modified. An orange-colored zone of "amorphous" material forms around the reagent fragment. After standing a sufficient time to permit the separation of disks of the nickel-mercury thiocyanate, there will be found golden-orange spherulites interspersed among the almost colorless disks of the nickel salt.

With platinum present as chloroplatinic acid, the golden orange or yellow mossy dendrites of the gold compound are still present, but are less "mossy." In some concentrations, on long standing trichites appear and potassium chloroplatinate is precipitated. It is therefore good practice always to employ sodium mercuric thiocyanate as reagent when the presence of members of the platinum group is suspected.

### C. Detection through Reduction to Colloidal Gold (Purple of Cassius).

(a) Method of Cole.<sup>22</sup>—To the test drop, which should be as free as possible from  $\text{HNO}_3$  and  $\text{HCl}$ , add a  $\text{SnCl}_2$ -pyrogallol impregnated viscose-rayon fiber about 5 mm. long, laying it half in, half out, of the test drop. Examine it from time to time, allowing the drop to pass completely to dryness by spontaneous evaporation. If gold is present, the fiber turns red, violet, or blue, depending upon concentrations.

Free mineral acids greatly retard the reaction. Alkalis and oxidizing agents must be absent. Compounds that react energetically with  $\text{SnCl}_2$  must also be absent.

Silver imparts a brown color to the fiber when in large amount, but does not mask the color of the gold unless the latter is present only in traces. Chromates, bichromates, and permanganates color the fiber brown, and if gold is also present the color of the fiber becomes a brownish red or purple, rendering the interpretation of the test doubtful.

Molybdates color the fiber blue but never bluish-red, violet, or red.

The bluish-red, violet, or red color appears to be specific for gold, and permits the detection of gold in the presence of chlorides of the other elements.

The metals of the platinum group do not interfere.

The reagent fibers are prepared as follows:

"10 grams of  $\text{SnCl}_2$  crystals are dissolved in 95 cc. of distilled  $\text{H}_2\text{O}$  and 5 cc. concentrated  $\text{HCl}$ , and filtered; 10 grams of white pyro-

<sup>22</sup> *Philippine Jour. Sci.* 21, 361 (1922).



gallol are added to the filtrate, a little at a time, with constant stirring. Fine viscose-rayon fibers are introduced into the solution and the preparation is heated on the water bath for ten minutes. The fibers are then removed, washed well with distilled water, and dried by pressing between filter paper."

The fibers thus treated keep well and are very sensitive.

(b) Method of Donau.<sup>23</sup> — Raw, true silk fibers are purified by being soaked in 10 per cent KOH for several hours, washed thoroughly, and then treated with  $\text{SnCl}_2$  and pyrogallol as described above, washed, dried, and used to test for gold. The behavior of the treated fiber in the presence of gold is exactly the same as that of the viscose-rayon fiber, but the latter is more sensitive and can be kept in serviceable condition for a longer time.

#### D. By Means of Thallous Nitrate — $\text{TlNO}_3$ .

*Compound Formed* —  $\text{TlAuCl}_4 \cdot 5 \text{H}_2\text{O}$ .

If the material to be tested has been brought into solution with aqua regia, it should be evaporated repeatedly with concentrated HCl to drive off all  $\text{HNO}_3$ . The solution is then carefully evaporated substantially to dryness to free it from HCl.

To the faintly yellow test drop, add several crystals of  $\text{TlNO}_3$ . The reagent almost immediately becomes covered with a coating of bristling yellow needles which rapidly grow into long thin prisms with oblique ends. Lemon-yellow rhombiform plates also abound; they have an acute angle of about  $82^\circ$  and extinguish at an angle of approximately  $28^\circ$  with their elongation. Short stout prisms with beveled or truncated ends are formed on long standing. Often, remarkable very long and curving trichites are obtained (Fig. 180, page 287).

In view of the large number of double chlorides into the composition of which thallium enters, this beautiful reaction has little value in the routine analysis of unknown substances. It is useful as a confirmatory test when applied to material which has been isolated by processes yielding a gold salt freed from most impurities.

Platinum and iridium give exceedingly minute octahedra.

Palladium gives radiates, stars, and lichen-like masses. (See Palladium, page 294.)

E. By Means of Silver Nitrate and Rubidium Chloride. — (See page 80.)

<sup>23</sup> *Monatsh.* 25, 545 (1904).

## DETECTION OF THE RARE EARTHS

This group of rare elements, whose properties place them in the Third and Fourth Groups of the Periodic System but whose atomic weights (in part) require that they be set apart in a series by themselves, constitute one of the most intricate and difficult separation problems confronting the chemist-analyst. Several of the now so-called "elements" in the series are probably not simple substances, and it is doubtful whether any of them have been prepared in a really pure state.

	La 139	Ce 140	Pr 141
Nd 144		Sm 150	Eu 152
Gd 157	Tb 159	Dy 162	Ho 163
Er 168	Tu 169	Yb 174	Lu 175

The relationships of those of the "rare earth" not found in the Periodic Classification of the Elements as shown on page 427 can be expressed by the above tabulation. The atomic weights, as given, are approximate only.

If the problem of separation and identification is so difficult on a large scale that chemists have struggled with it for many years with only a modicum of success, how infinitely more complicated must the problem be when attempting analyses on a "micro" scale.

Many excellent separation methods have been described, but none are sharp. None of the precipitations are quantitatively complete; always a little of the precipitated substance is left behind in solution and always the precipitate carries down with it other substances. Thus the purification methods at our command must be, for the most part, some system of fractionation, but fractionating of the kind required is impracticable when dealing with very small amounts of material.

It is true that Behrens has reported<sup>24</sup> that he had considerable success in identifying a number of the rare earths by microscopical reactions, and that R. J. Meyer<sup>25</sup> has been similarly optimistic; but we have had doubtful success, even though one of us has had some years of experience in "rare-earth" research.

<sup>24</sup> Behrens: Ein Beitrag z. Kenntnis d. Metalle d. Ceriumgruppe. *Arch. néerland.* (2) 6, 67 (1902). See also Behrens-Kley, *op. cit.*

<sup>25</sup> Meyer, R. J.: Der mikroskopische Nachweis d. selten Erden. *Zeit. f. anorg. Chem.* 33, 31 (1902).

There is no question that most of the individual substances composing the group commonly termed the "rare earths" when tested in the form of their "pure" salts give crystal reactions sufficiently different in character to enable an experienced analyst to differentiate between them. He may even be successful when dealing with mixtures he has made up. But it is a very different matter when the analyst is confronted with materials of which he has no previous knowledge.

We must still have recourse to the spark, arc, and absorption spectra, or to X-ray spectrographic methods, for the identification of the "rare earths." The "earths" are too closely related and form isomorphous mixtures far too readily to permit dependable identification methods to be based upon crystal habit and optical properties.

Because the authors do not consider the known "micro" tests sufficiently trustworthy in the case of the "rare-earth" group as a whole, they have given below a mere outline of properties, crystal habits, and separation methods.

Classification.

<i>Cerium Group</i>	$\left\{ \begin{array}{l} \text{Scandium} \\ \text{Thorium} \\ \text{Lanthanum} \\ \text{Cerium} \\ \text{Praseodymium} \\ \text{Neodymium} \\ \text{Samarium} \\ \text{Erbium} \\ \text{Holmium} \end{array} \right\}$	Sulphates practically insoluble in saturated solution of $\text{K}_2\text{SO}_4$
<i>Terbium Group</i>	$\left\{ \begin{array}{l} \text{Europium} \\ \text{Gadolinium} \\ \text{Terbium} \\ \text{Samarium} \end{array} \right\}$	Sulphates moderately soluble in saturated solution of $\text{K}_2\text{SO}_4$
<i>Yttrium Group</i>	$\left\{ \begin{array}{l} \text{Yttrium} \\ \text{Ytterbium} \\ \text{Lutecium} \end{array} \right\}$	Sulphates readily soluble in saturated solution of $\text{K}_2\text{SO}_4$

### Preliminary Treatment of Rare Earth Material

Bring the material into solution by direct action of  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , or aqua regia, or by solution in one of these acids after fusing with a suitable fusing mixture.

Precipitate the earths with  $\text{NH}_4\text{OH}$ . Filter and wash thoroughly. Dissolve the washed hydroxides in a platinum dish in a mixture of  $\text{HCl}$  and  $\text{HF}$ , equal parts, diluted to about 1 : 5. Evaporate to dryness on the water bath. The residue is digested with the  $\text{HCl}$ - $\text{HF}$  mixture and filtered, using a hard rubber, Bakelite, or other "plastic" funnel. The insoluble material thoroughly washed with a dilute  $\text{HCl}$ - $\text{HF}$  mixture contains all the rare earths having atomic numbers 21, 39, 57 to 71, inclusive, and 90, as fluorides but no other elements save indium and uranium, which may be co-precipitated in part under certain condi-

tions.<sup>26</sup> The earth fluorides thus separated are brought into solution by heating with concentrated  $\text{H}_2\text{SO}_4$  until fumes are evolved. The mass is dissolved in water, diluted, again precipitated with  $\text{NH}_4\text{OH}$ , and the washed hydroxides dissolved in  $\text{HCl}$ .

It is customary to start with precipitation by an excess of oxalic acid in a solution rather strongly acidified with  $\text{HCl}$ . The precipitation is not complete.

The filtered and well-washed oxalates are ignited and the oxides dissolved in  $\text{HNO}_3$ .

A number of the "rare earths" can be identified by their absorption spectra. The observations can be made by light transmitted through their solutions, through their crystals, or by observations made upon light reflected from them in the solid or liquid state.

It must be borne in mind, however, that the absorption spectra of different salts of the same "earth" will vary unless the dilution is great, and that an excess of acid in the solutions will displace the absorption bands.<sup>27</sup>

Dysprosium, Erbium, Europium, Gadolinium, Holmium, Neodymium, Praseodymium, Samarium, and Thulium give absorption bands.

The wavelengths in Ångström units of the most important of these bands are as follows:

Dysprosium (Chloride):

4740; (4530-4500); (Urbain)

Erbium (Nitrate): 16 bands.

5232; 4875; 4499; (Formànek)

Europium:

5900; 5700; 5350; 5250;

4690; 3995; 3855; (Demarçay)

Gadolinium (Nitrate):

(3500-3390); (3300-2890); (2200) (H. D. Jones)

Holmium (Nitrate):

6405; 5363; (Dennis and Dales)

Neodymium (Nitrate); 9 bands:

7291; (5979-5759); (5222-5209); 4277; (Formànek)

Thulium (Nitrate):

6832; (Dennis and Dales)

Since uranium is very apt to be present in "rare-earth" solutions, unless special precautions have been taken to eliminate it, the analyst should be on his guard so as to recognize the absorption spectrum of its nitrate solution.

Uranium (Nitrate):

4705; 4867; 4545; 4425; 4290; 4150; (Formànek)

<sup>26</sup> See Lundell and Hoffman: *Outlines of Methods of Chemical Analysis*, p. 86.

<sup>27</sup> See Kayser: *Handbuch der Spectroscopie* III, 427-453. (Hirzel, Leipzig, 1905).  
Formànek: *Die qual. Spektralanalyse anorganische Körper*, (Mückenberger, Berlin, 1900).

Baly, E. C. C.: *Spectroscopy* (Longmans, N. Y., 1924).

One of the most comprehensive of the many separation schemes which have been proposed is that of Noyes and Bray.<sup>28</sup>

Only that part dealing with the "rare earths" is here given:

The earths are converted into insoluble fluorides by HF.

The insoluble "rare-earth" fluorides are treated with HF containing an excess of  $\text{NH}_4\text{F}$ .

Scandium fluoride is dissolved.

The insoluble fluorides are treated with concentrated  $\text{H}_2\text{SO}_4$ , heated until  $\text{SO}_3$  fumes appear, water added and  $\text{NH}_4\text{OH}$  added in slight excess. Filter, wash, and dissolve the precipitate in  $\text{HC}_2\text{H}_3\text{O}_2$ . Evaporate, add  $\text{HNO}_3$ ,  $\text{KClO}_3$ , and  $\text{KIO}_3$ .

$\text{ThIO}_3$ ,  $\text{CeIO}_3$  are precipitated. Filter.

To the filtrate from thorium and cerium add  $\text{NH}_4\text{OH}$ , filter, dissolve in  $\text{HCl}$ , and add  $\text{K}_2\text{CO}_3$ .

Double carbonates of La, Pr, Nd, Sm, Eu, Y, Yb, Lu are precipitated. The salts precipitated have the general formula  $\text{K}_2\text{CO}_3 \cdot \text{MCO}_3$ .

The solution from the  $\text{K}_2\text{CO}_3$  solution contains Y group, Gd, Tb, Dy, Ho, Er, Tu, Yb, Lu and traces of Nd, Sm, Eu.  $\text{HCl}$  is added and  $\text{NH}_4\text{OH}$ . The precipitate formed is dissolved in  $\text{HCl}$ , evaporated, and formic acid and ammonium formate added.

Nd, Sm, Eu are precipitated as formates together with some of the yttrium group.

Y, Yb, Lu form soluble formates and remain in solution.

The further separation as advocated by Noyes and Bray, by fusion with  $\text{NaNO}_3$ , is impracticable on a micro scale. But partial separations by fusions with sodium nitrate are practicable if applied to the original material, providing this consists of about half a gram or more. Convert the oxides or hydroxides into double ammonium nitrates. Mix these double salts with about six times their weight of a fusing mixture consisting of equal parts of anhydrous  $\text{KNO}_3$  and  $\text{NaNO}_3$ . Fuse at  $350^\circ\text{C}$ . for not less than one hour. All the iron and cerium will have been rendered insoluble in water. Dissolve in warm water and thoroughly extract the insoluble residue with a concentrated solution of  $\text{NH}_4\text{NO}_3$ . Evaporate to dryness the united extracts. Thoroughly dry this residue and fuse at  $415^\circ\text{C}$ . Substantially pure praseodymium oxide is obtained as a black residue insoluble in water and free from lanthanum.

Behrens states that the best reagent for the separation of neodymium from praseodymium is by fractionating cerium-free material with ammonium succinate in nitrate or chloride solutions.

<sup>28</sup> *Op. cit.*

The precipitate obtained consists in

- Fraction I, of Nd and much Sm
- II, almost entirely of Nd
- III, of Nd and Pr, and a little Sm
- IV, almost entirely of Pr
- V, of Pr and La

The reagents which have been proposed for the "micro" identification of "rare earths" are as follows:

- Ammonium succinate
- Formic acid and ammonium formate
- Iodic acid and potassium iodate
- Lactic acid
- Oxalic acid
- Potassium carbonate
- Potassium ferrocyanide
- Potassium sulphate

None of these reagents give sharp definite reactions with mixtures of the "rare earths."

It is imperative that the analyst shall have experimented with pure materials and with mixtures and that he shall have conscientiously carried through the various separation methods if he is to avoid serious errors when dealing with materials of wholly unknown "rare-earth" content.

The authors are inclined to go a step farther and state that until an analyst has obtained and worked upon materials of which he himself knows nothing but whose composition is known to others so that he can thus check his findings, he should not have the temerity to attempt a qualitative analysis of "rare earths," minerals, or products.

A most interesting partial separation of the rare earths has been found by Goswami and Sarkar<sup>29</sup> and is based upon the insolubility of certain triple nitrites. We are including it in our discussion of the rare earths because it has a very direct bearing upon the discussion of the triple nitrite reactions on pages 207-209.

To a small volume of 50 per cent solution of rare-earth nitrates add an equal volume of 50 per cent sodium nitrite solution. Filter and to the filtrate add about half its volume of a 10 per cent solution of  $\text{CsNO}_3$ ; a precipitate of tiny isotropic octahedra is formed with La, Ce, Pr, Nd, Sm, Eu, Gd; but not with Tb, Dy, Ho, Er, Tm, Yb, Lu.

The compounds formed are said to have the formula  $\text{CsNa}(E^{+++})-$

<sup>29</sup> *Jour. Indian Chem. Soc.* 12, 608 (1935).

(NO<sub>2</sub>)<sub>4</sub>, where  $E^{+++}$  may be any one of the earths having atomic numbers 57 to 64 inclusive.

The latest search for procedures for the microscopical separation and identification of the rare earths by Martini<sup>30</sup> led him to the conclusion that at that time (1937) there existed no specific tests for the earth cations studied, nor were more satisfactory group reactions found than those already in use.

<sup>30</sup> *Publ. d. Instit. d. Invest. Microquim.* 1, 71 (1937), (Argentina).

## CHAPTER XI

### THE DETECTION OF ANIONS

The identification of the anion of a salt is more difficult and more complicated than is the search for its cation, and in mixtures the problem becomes even more intricate and is almost sure to tax the chemical knowledge and resourcefulness of the analyst.

Tests for cations are ordinarily quite specific and an "element" can be readily detected, no matter with what "acid" it is combined; but there are fewer specific tests for anions as such and there is the possibility of conversion to another anion. Moreover, the behavior of an anion toward reagents is largely influenced by the nature of the cation with which it is combined, so that the identification of the anion of a given salt must not infrequently turn upon the identification of its cation also, before the problem can be solved.

The problem becomes even more involved when the analyst is confronted with the task of devising a means of identifying a complex ion and of deciding whether he has to deal with a true double salt or a complex.

For the purposes of qualitative analysis, the "elements" can be classified into relatively small and quite distinctive groups, but such distinctive groupings are not practicable with the acids. Even the most satisfactory of these — the Bunsen-Treadwell classification — leaves much to be desired.

Wholly aside from the absence of satisfactory "Tables" for the detection of the anions, and the lack of specific identity tests, their recognition is the more difficult when the analyst bases his deductions wholly upon the properties of the cations he has found, and fails to consider the probable chemical behavior of the compound in question in its entirety. This may, perhaps, be a distinction too finely drawn, but it is nevertheless quite germane to the problem and always has a decided bearing upon the solution of a complex analytical problem.

A further caution is necessary in testing for anions. The analyst must not fail to consider the possibility of a reaction between a cation in the unknown and an anion in the reagent. For example, when using the Bunsen-Treadwell classification the addition of  $\text{BaCl}_2$  may cause a precipitate of chlorides of  $\text{Ag}^+$ ,  $\text{Pb}^{++}$ ,  $\text{Hg}^+$ , or  $\text{Tl}^+$ , and such a precipi-



tate may be mistaken for an insoluble or difficultly soluble salt of  $Ba^{++}$ . The analyst may thus be led into the error of concluding that an anion is present which gives a precipitate with  $Ba^{++}$ .

In general the identification of cations must go hand in hand with the detection of anions. It is never safe to base conclusions upon results obtained by blindly following a "scheme" of analysis.

The recognition of the true nature of a given crystalline compound lies not so much in the identification of the cations and anions present as in reaching a decision as to exactly how they are combined; in other words, is the material a mechanical mixture, an isomorphous mixture, a double or a mixed salt, or a salt containing complex ions? The solution of the problem rests as much or more upon physicochemical experiments and crystallographic properties as upon the addition of reagents. This phase has already been discussed in *Vol. I*, page 354, to which the reader is referred.

The problem of complex ions is not easily solved. There are many reasons for believing that their existence in materials is much more general than is commonly supposed. In many instances an equilibrium exists between the complex ion and the simple anions and cations which compose it, so that either may be exhibited in analytical testing. The effective concentrations of a number of anions may be markedly lowered by their being "locked up" in complex ions; the complexes may dissociate partially, according to the mass law, if the concentration of the simple anion is lowered. The analyst must be guided by his general knowledge of chemistry, by the properties of the compound in hand, or by actual experimental electrolysis. Unfortunately the latter can be successfully undertaken by experienced workers only, and is fraught with complications. We still lack data in many cases as to whether a compound is a double salt or a salt of a complex ion.

To facilitate discussion and expedite analyses, the authors have adopted the Bunsen-Treadwell classification of the acids. This classification is based upon the behavior of the commoner anions toward silver nitrate and toward barium chloride in neutral and in nitric acid solutions.

No system based upon solubilities can be wholly satisfactory. A very minute amount of a precipitate recorded as "slightly" soluble may appear to be "readily" soluble if treated with sufficient solvent to bring it into solution. Moreover, an "insoluble" precipitate may be peptized by materials present and thus appear to be soluble. Furthermore, extremely high concentrations may result in precipitates of salts which would normally be considered readily soluble.

An equal difficulty arises in regard to the color of a precipitate, for

if but faintly colored and in small amount the precipitate will not be recognized as colored. A good example is  $\text{AgI}$ , which is so faintly yellow that in "micro" amounts it will be classed as colorless. Faint colors must be observed by reflected light after the precipitate formed has been collected into a little heap. This can usually be accomplished by pushing the precipitate together so as to mass it just outside the circumference of the drop, using a drawn-out glass rod or tiny platinum spatula for the purpose. It is best to compare appearances upon a white and upon a dark background. The variety of colors listed for each precipitate may be ascribed to the range of particle-size. The first particles to separate are likely to be so fine as to appear very pale in hue even when larger crystals are intensely colored or almost opaque.

### SILVER NITRATE GROUP I

*The Silver Salt Is Insoluble in Water and in Strong Nitric Acid, and Is Not Perceptibly Crystalline Nor Colored.*

$\text{Cl}^-$	Chloride	May separate in crystals recognizable as tiny octahedra.
$\text{BrO}_3^-$	Bromate	May separate in crystals recognizable as tiny crosses and prisms.
$\text{Br}^-$	Bromide	Granular, or very tiny octahedra.
$\text{CN}^-$	Cyanide	Granular or fine prisms.
$\text{I}^-$	Iodide	Granular.
$\text{OCl}^-$	Hypochlorite	Silver hypochlorite is soluble in water, but through decomposition $\text{AgCl}$ and $\text{AgClO}_3$ are formed.
$\text{Fe}(\text{CN})_6^{4-}$	Ferrocyanide	Precipitate turns red or brown with $\text{HNO}_3$ .
$\text{SCN}^-$	Thiocyanate	Precipitate soluble in conc. $\text{HNO}_3$ but not in dilute.

### SILVER NITRATE GROUP II

*A Colored Precipitate Is Formed upon the Addition of Silver Nitrate.*

(a) The precipitate is red or brown.

$\text{AsO}_4^{3-}$	Arsenate (ortho)	Granular; irregular cryst. grains; plates and tablets; dendritic masses. Difficultly soluble in cold $\text{HNO}_3$ ; readily soluble in hot $\text{HNO}_3$ . Soluble in $\text{NH}_4\text{OH}$ .
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$\text{CrO}_4^{--}$ ; $\text{Cr}_2\text{O}_7^{--}$	Chromate; Bichromate	Granular; rectangular and non-symmetrical 6-sided plates; acute rhombs; aggregates of pleochroic broken scales; difficultly soluble in cold $\text{HNO}_3$ . Soluble in hot $\text{HNO}_3$ . Soluble in $\text{NH}_4\text{OH}$ .
$\text{Fe}(\text{CN})_6^{--}$	Ferricyanide	"Amorphous." Difficultly soluble in $\text{HNO}_3$ .
$\text{IO}_4^-$	Periodate	Yellow at first, becoming brown; hexag. rosettes and platelets.
$\text{S}_2\text{O}_3^{--}$	Thiosulphate	White "amorphous" ppt. changing to yellow, then to dark brown ( $\text{Ag}_2\text{S}$ ). Solubility in $\text{HNO}_3$ indeterminate owing to presence of precipitated sulphur.
$\text{S}^{--}$	Sulphide	Brown, becoming black. "Amorphous." Soluble in $\text{HNO}_3$ .
$\text{MnO}_4^-$	Permanganate	Solution was pink or red. From very concentrated solutions a black cryst. ppt. Thin plates violet-red.
$(\text{H}_2\text{PO}_2)^-$	Hypophosphite	There is first formed a heavy white "amorphous" or granular ppt. which turns brown or black ( $\text{Ag}$ ).

(b) The precipitate is yellow.

$\text{AsO}_2^-$ ; $\text{AsO}_3^{--}$	Arsenate	"Amorphous"; granular or acicular; soluble in $\text{HNO}_3$ .
$\text{Fe}(\text{CN})_6^{--}$	Ferricyanide	Rarely yellow, usually red or brown. "Amorphous." Difficultly soluble in $\text{HNO}_3$ .
$\text{IO}_4^-$	Periodate	Yellow, changing to brown on standing.
$\text{NO}_2^-$	Nitrite	Colorless needles unless in a mass, then yellowish green. Soluble in $\text{HNO}_3$ .
$\text{PO}_4^{--}$	Phosphate (ortho)	Granular; tiny dendritic stars, crosses, and radiates. Soluble in $\text{HNO}_3$ .
$\text{SiO}_3^{--}$	Silicates	May be yellow ppt. or ppt'g of $\text{Ag}_2\text{O}$ . If $(\text{SiO}_2)_x$ is precipitated, insoluble in $\text{HNO}_3$ . Colloidal $\text{Ag}$ may be formed.
$\text{VO}_3^-$ ; $\text{VO}_4^{--}$	Vanadates	"Amorphous"; readily soluble in $\text{HNO}_3$ .
$\text{S}_3\text{O}_6^{--}$	Trithionate	Yellow "amorphous" precipitate rapidly turning black even in dilute solutions.
$\text{S}_4\text{O}_6^{--}$	Tetrathionate	Same as trithionate.
$\text{S}_5\text{O}_6^{--}$	Pentathionate	Same as trithionate.

## SILVER NITRATE GROUP III

*A White or Colorless Precipitate Is Formed, and the Precipitate Is Soluble in Nitric Acid.*

(a) The precipitate is usually crystalline.

$(C_2H_3O_2)^-$	Acetate	Pearly scales, thin plates, and irregular prisms.
$(MoO_4)^-$ ?	Molybdate	"Amorphous" or granular.
$NO_2^-$	Nitrite	Long slender needles. Yellowish-green.
$(C_2O_4)^-$	Oxalate	Granular; hexagonal plates; prisms.
$S_2O_8^{2-}$	Persulphate	$Ag_2S_2O_8$ is readily soluble in water. The addition of $AgNO_3$ to the test drop is without effect for a few seconds; then there appears a copious separation of crystals of $Ag_2SO_4$ . Often the test drop turns brown, especially at its circumference.
$SeO_4^{2-}$	Selenate	Skeleton forms; rhombs; prisms.
$SO_4^{2-}$	Sulphate	Skeleton forms; rhombs; prisms.
$(C_4H_4O_6)^-$	Tartrate	Granular; rectangular tablets; short prisms.
$S_2O_3^{2-}$	Thiosulphate	First white, changing to yellow to brown ( $Ag_2S$ ). If much sulphur is set free ppt. will appear to be insoluble in $HNO_3$ .
$WO_4^{2-}$	Tungstate (ortho)	"Amorphous" or granular.

(b) The precipitate is not discernibly crystalline.

$B_2O_4^{2-}$ ( $BO_2^-$ ); $B_4O_7^{2-}$	Borates	"Amorphous," curdy; granular.
$CO_3^{2-}$	Carbonate	"Amorphous," granular; may become crystalline.
$CNO^-$	Cyanate	"Amorphous," becoming crystalline; fine needles; prisms.
$IO_3^-$	Iodate	"Amorphous." Acicular and radiating crystals in presence of $HNO_3$ .
$SO_3^{2-}$	Sulphite	White "amorphous" precipitate readily soluble in $HNO_3$ ; soluble in excess of alkali sulphite. On standing, $Ag_2SO_4$ separates from $SO_4^{2-}$ in sulphites, and oxidation by $AgNO_3$ .

## SILVER NITRATE GROUP IV

*The Silver Salt Is Soluble in Water.*

(a) No precipitate is formed even in concentrated solutions.

$\text{ClO}_3^-$	Chlorate	
$\text{ClO}_4^-$	Perchlorate	
$\text{F}^-$	Fluoride	Partly decomposed by water with precipitation of Ag.
$\text{MnO}_4^-$	Permanganate	$\text{AgMnO}_4$ separates from highly concentrated solutions.
$\text{NO}_3^-$	Nitrate	
$\text{S}_2\text{O}_6^{--}$	Dithionate	

(b) The silver salt has a solubility sufficiently low to separate from concentrated solutions.

$(\text{C}_2\text{H}_3\text{O}_2)^-$	Acetate	Pearly scales; thin plates, irregular prisms.
$\text{B}_2\text{O}_4^{--}; \text{B}_4\text{O}_7^{--}$	Borate	"Amorphous," curdy, granular.
$\text{SiF}_6^{--}$	Fluosilicate	Granular, becoming crystalline.
$\text{TiF}_6^{--}$	Fluotitanate	Granular, becoming crystalline.
$\text{ZrF}_6^{--}$	Fluozirconate	Granular, becoming crystalline.
$\text{SeO}_4^{--}$	Selenate	Skeleton forms, rhombs, prisms.
$\text{S}_2\text{O}_8^{--}$	Persulphate	A precipitate of $\text{Ag}_2\text{SO}_4$ is obtained. See Silver Nitrate, Group III, page 318.
$\text{SO}_4^{--}$	Sulphate	Skeleton forms; rhombs; prisms.

## BARIUM CHLORIDE GROUP I

*The Barium Salt Is Insoluble in Water, and Insoluble in Nitric Acid.*

$\text{CrO}_4^{--}; \text{Cr}_2\text{O}_7^{--}$	Chromate; Bichromate	$\text{BaCrO}_4$ is difficultly soluble in $\text{HNO}_3$ . Granular, becoming crystalline; dendritic.
$\text{SiF}_6^{--}; \text{TiF}_6^{--}; \text{ZrF}_6^{--}$	Fluosilicate; Fluotitanate; Fluozirconate	Difficultly soluble in $\text{HNO}_3$ . Crystalline prismatic grains; spherocrystals, sheaves.
$\text{NO}_3^-$	Nitrate	$\text{Ba}(\text{NO}_3)_2$ is almost insoluble in $\text{HNO}_3$ , and of low solubility in water; crystals may separate from concentrated solutions and will not dissolve in $\text{HNO}_3$ . Isotropic octahedra.

$\text{IO}_3^-$	Iodate	Granular; fine prisms and crosses; difficultly soluble in $\text{HNO}_3$ .
$\text{SO}_4^{--}$	Sulphate	Granular, becoming crystalline plates, tablets, skeleton crystals.
$\text{SeO}_4^{--}$	Selenate	Similar to $\text{SO}_4^{--}$ .
$\text{WO}_4^{--}$	Tungstate (ortho)	"Amorphous," granular. $\text{WO}_3$ is precipitated by $\text{HNO}_3$ .

## BARIUM CHLORIDE GROUP II

*The Barium Salt Is Insoluble in Water but Is Soluble in Nitric Acid.*

$\text{AsO}_4^{--}$	Arsenate (ortho)	"Amorphous"; obtained in concentrated solutions only.
$\text{B}_2\text{O}_4^{--}(\text{BO}_2^-)$ ; $\text{B}_4\text{O}_7^{--}$	Borates	"Amorphous"; granular.
$\text{BrO}_3^-$	Bromate	From concentrated solutions. Prisms.
$\text{CO}_3^{--}$	Carbonate	Curdy, becoming crystalline; variable.
$\text{CrO}_4^{--}$ ; $\text{Cr}_2\text{O}_7^{--}$	Chromate; Bichromate	Bright <u>yellow</u> , granular. Soluble in $\text{HNO}_3$ with difficulty.
$\text{CNO}^-$	Cyanate	Disks, sphero-crystals, aggregates of fine needles.
$\text{F}^-$	Fluoride	Granular.
$\text{SiF}_6^{--}$ ; $\text{TiF}_6^{--}$ ; $\text{ZrF}_6^{--}$	See Group I.	
$(\text{HPO}_3)^-$	Phosphite	Disks, crystalline grains.
$\text{IO}_3^-$	Iodate	Granular; stars; dendrites. Difficultly soluble in $\text{HNO}_3$ .
$(\text{MoO}_4)^{--}?$	Molybdate	"Amorphous," granular.
$(\text{C}_2\text{O}_4)^-$	Oxalate	Granular; dendritic.
$\text{PO}_4^{--}$	Orthophosphate	"Amorphous," granular.
$\text{PO}_3^-$	Metaphosphate	Trace of precipitate.
$\text{P}_2\text{O}_7^{--}$	Pyrophosphate	Gelatinous.
$\text{SO}_3^{--}$	Sulphite	Granular, becoming crystalline; dendritic.
$\text{S}_2\text{O}_8^{--}$	Persulphate	Precipitate in concentrated solutions only. May appear to be insoluble in $\text{HNO}_3$ because of presence of $\text{SO}_4$ .
$\text{WO}_4^{--}$	Tungstate (ortho)	"Amorphous," granular. $\text{HNO}_3$ causes separation of $\text{WO}_3$ .

## BARIUM CHLORIDE GROUP III

*No Precipitate Is Obtained When Barium Chloride Is Added to a Dilute Aqueous Solution.*

$(C_2H_3O_2)^-$	Acetate	
$AsO_4^{3-}$	Arsenate (ortho)	A precipitate is obtained in moderately concentrated solutions.
$AsO_2^-; AsO_3^{3-}$	Arsenites	
$BrO_3^-$	Bromate	Precipitate in concentrated solutions. Prisms.
$Br^-$	Bromide	
$ClO_3^-$	Chlorate	
$Cl^-$	Chloride	
$CNO^-$	Cyanate	Solubility low. Precipitate in moderately concentrated solutions.
$CN^-$	Cyanide	Solubility low.
$Fe(CN)_6^{3-}$	Ferri cyanide	
$Fe(CN)_6^{4-}$	Ferrocyanide	Precipitate of prisms and tablets in moderately concentrated solutions.
$(H_2PO_2)^-$	Hypophosphite	
$I^-$	Iodide	
$NO_3^-$	Nitrate	$Ba(NO_3)_2$ is difficultly soluble and may separate from concentrated solutions.
$NO_2^-$	Nitrite	
$S_2O_8^{2-}$	Persulphate	Solubility low. May precipitate.
$PO_3^{3-}$	Metaphosphate	
$(C_4H_4O_6)^-$	Tartrate	Solubility low. May precipitate.
$SCN^-$	Thiocyanate	
$S_2O_3^{2-}$	Thiosulphate	A precipitate in all but very dilute solutions.
$S_2O_8^{2-}$	Dithionate	No precipitate even in concentrated solutions.
$S_3O_6^{2-}$	Trithionate	Like dithionate.
$S_4O_6^{2-}$	Tetrathionate	Like dithionate.
$S_5O_6^{2-}$	Pentathionate	Like dithionate.

Before testing with  $AgNO_3$  or  $BaCl_2$ , two very important steps are essential if time is to be saved and trouble avoided. First: Determine the reaction of the solution to litmus. Free acids and free alkalis do not fall within the scope of the above groups. Second: Attempt to

obtain good crystals from the material in question and ascertain their behavior between crossed nicols. (See *Vol. I*, Chapter IX.)

In the end, the *real identification* of the salt must rest largely upon its optical properties, for the mere detection of cations and anions in solution usually gives inadequate information as to the actual solid salt in hand. There may exist a number of distinct hydrates, and in double salts there may exist several combinations in which the ratios of one component to the other are very different. (See *Vol. I*, pages 340, 354.) Optical tests alone cannot, however, be the sole criteria upon which a final decision is based, except in special cases.

Free acids should first be converted into salts by evaporating with  $\text{NH}_4\text{OH}$ , if practicable; if not, by careful neutralization with  $\text{NaOH}$  and evaporation.

Alkaline hydroxides are recognized through their general behavior, their strong alkaline reaction, their precipitation of  $\text{Ag}_2\text{O}$  or a hydrous oxide, and the identification of the metallic element present.

Having obtained an indication as to what anions are possibly present, apply to a series of test drops a specific test for each anion that may be present. In dealing with mixtures, separations of groups may be advantageous; these may be carried out macroscopically, or by means of microfiltrations, decantation, distillation, etc.

**Borates** —  $\text{BO}_2^-$ ,  $\text{B}_4\text{O}_7^{--}$ . — All borates are at least slightly soluble in water; those of the alkalis are readily soluble. The borates of the alkaline earths are as a rule more soluble in cold than in hot water.

The borates with which the analyst will come in contact are derived from orthoboric acid  $\text{H}_3\text{BO}_3$ , metaboric acid  $\text{HBO}_2$ , and pyroboric or tetraboric acid  $\text{H}_2\text{B}_4\text{O}_7$ . Few orthoborates are known; hence practically all borates commonly met with are meta- or pyro-borates.

With the exception of the alkali borates, few borates are stable in solution.

The detection of borates turns upon the identification of boron by means of viscose-rayon fibers impregnated with turmeric. (See Boron, page 170.)

An indication of the possible presence of boron can be obtained when testing concentrated solutions with  $\text{NH}_4\text{F} \cdot \text{HF}$  or with  $\text{HF}$  (see pages 62, 171, 190) or upon the addition of  $\text{HCl}$  (see page 174).

(a) Group Reaction.

1. With  $\text{AgNO}_3$  in all but very dilute solutions there is immediately formed a white curdy "amorphous" precipitate having a tendency to become granular, but no definite crystals are formed.

2.  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  yields nothing more than a white granular precipitate not perceptibly crystalline under magnifications up to  $300\times$ .



3.  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  produces no precipitate save in very concentrated solution, and then a slight turbidity results after standing for a short time.

4.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives a curdy white precipitate, becoming granular.

5.  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$  produces no precipitate and no crystals separate on standing.

6.  $\text{HgCl}_2$ , added by Method I, page 31, to an aqueous solution of a borate, produces a yellow-to-red granular precipitate or yellow-to-red plates or disks. The precipitate becomes brown on standing.

**Carbonates** —  $\text{CO}_3^{--}$ ;  $(\text{HCO}_3)^-$ . — The carbonates of sodium and those of the Potassium Group are readily soluble in water.  $\text{Li}^+$  and  $\text{Tl}^+$  form somewhat difficultly soluble carbonates. The normal carbonates of most of the other elements are either insoluble or difficultly soluble in water, but are partly (sometimes completely) soluble in water charged with  $\text{CO}_2$ , owing to their conversion into "bicarbonates," i.e., salts of the anion  $(\text{HCO}_3)^-$ .

The carbonates of  $\text{NH}_4^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  are easily soluble in alcohol but none of the other common carbonates are soluble in this liquid.

The detection of carbonates is based upon the fact that they are readily transformed by acids,  $\text{CO}_2$  being given off with effervescence.

The test for effervescence is made as described on page 40. Merely the appearance of gas bubbles in the gelatin cannot be taken as proof of the presence of  $\text{CO}_2$ .  $\text{CO}_2$  must be tested for by evolution and absorption in a hanging drop of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ . Absorption in a solution of this reagent gives rise to the formation of acicular crystals, singly and in irregular aggregates, globulites or highly refractive rhomboidal grains.

Cyanates may also give off  $\text{CO}_2$  when treated with an acid.

When dealing with a solution, one or more drops should be evaporated to dryness in the crucible (see Fig. 10, page 17), covered with asbestos fibers, acid added, and the  $\text{CO}_2$  evolved tested with  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ .

*(a) Group Reactions.*

1. With  $\text{AgNO}_3$  both carbonates and bicarbonates yield a heavy white "amorphous" precipitate, soon becoming granular; in the outer zone, tiny, colorless, angular grains appear, and the outer edge of the precipitate mass becomes distinctly granular. In a number of restricted areas, disks, rosettes, and hexagonal plates are formed but these crystals always remain very small. They are, however, highly refractive and strongly birefringent. As the test drop passes to dryness, the mass of "amorphous" precipitate acquires a distinct cream color, owing to the formation of a small amount of  $\text{Ag}_2\text{O}$ .

2. With  $(\text{HCO}_3)^-$ ,  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives a slight sandy precipitate

consisting of tiny crystalline grains of irregular shape; but with  $\text{CO}_3^{--}$  there is first formed a thick, heavy, somewhat curdy precipitate in which crystallization starts almost at once. Tiny crystalline grains are formed and moss-like, many-branching, radiating dendritic aggregates. Tiny dendritic masses are also abundant.

3.  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives no precipitate, and no crystals separate on standing when the reagent is added to solutions of alkali bicarbonates; but with normal carbonates ( $\text{CO}_3^{--}$ ), a white flocculent "amorphous" precipitate is obtained that rapidly changes into very tiny rhombohedra. Eventually the entire precipitate becomes converted into strongly birefringent crystalline granules (Fig. 74, page 109).

4.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  does not differentiate between  $\text{CO}_3^{--}$  and  $(\text{HCO}_3)^-$  save that in the latter case the development of recognizable crystal forms is more rapid and the aggregates are of larger size. A heavy white "amorphous" precipitate is first formed. Tiny, irregular, colorless crystalline grains appear and tiny dendritic aggregates can be found in certain small areas. These branching aggregates become more and more numerous and assume shapes more like tufts of grass than moss, that is to say, that the branches are straighter and smoother than in a moss-like clump. They are also more fan-shaped, and are therefore one-sided radiates.

5.  $\text{Ti}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives no precipitate and no separation of crystals with  $(\text{HCO}_3)^-$ , but with  $\text{CO}_3^{--}$ , colorless, long slender needles are formed that soon stretch completely across the field (Fig. 190, page 325). These needles may become prismatic and extinguish at about  $5^\circ$  with their elongation. Long slender thin plates with terminal angles of about  $80^\circ$  are also formed. The crystals are highly refractive, strongly birefringent, and exhibit brilliant polarization colors. They are more soluble than the acicular crystals obtained with  $\text{PO}_4^{--}$  (Fig. 199, page 337), are formed more slowly as a rule, and tend to separate at the circumference of the test drop rather than at the zone of entrance of the reagent. Obviously the differences in the phenomena observed will depend upon relative concentrations.

#### DETECTION OF THE ANIONS OF THE NITROGEN GROUP

$\text{NO}_3^-$ ,  $\text{NO}_2^-$ ;  $\text{CN}^-$ ;  $\text{CNO}^-$ ;  $\text{SCN}^-$ ;  $\text{Fe}(\text{CN})_6^{--}$ ;  $\text{Fe}(\text{CN})_6^{--}$

Logically these ions should be discussed as four separate groups: (1)  $\text{NO}_3^-$  and  $\text{NO}_2^-$ ; (2)  $\text{CN}^-$  and  $\text{CNO}^-$ ; (3)  $\text{SCN}^-$ ; (4)  $\text{Fe}(\text{CN})_6^{--}$  and  $\text{Fe}(\text{CN})_6^{--}$ ; actually they have little in common and form five groups from the viewpoint of microscopical qualitative analysis.

**Nitrates** —  $\text{NO}_3^-$ . — All normal nitrates are water-soluble. Most basic nitrates are difficultly soluble or insoluble. A few normal nitrates

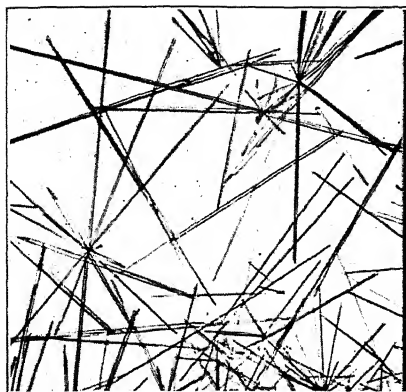


FIG. 190.  $\text{CO}_3^{--}$  with Thallous Acetate. 50 $\times$ .

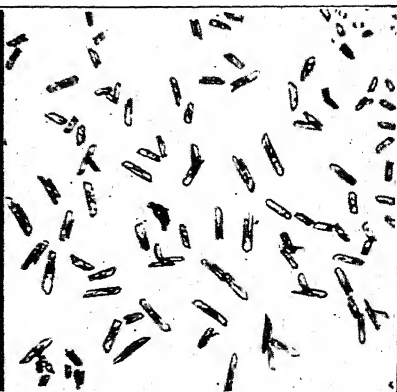


FIG. 191.  $\text{CN}^-$  with Silver Nitrate. 300 $\times$ .

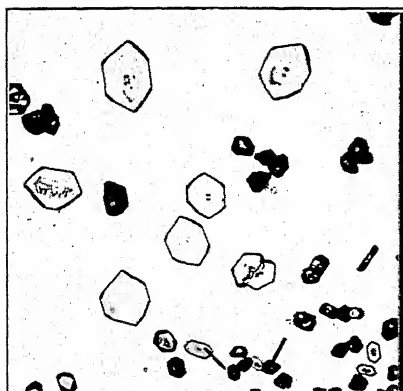


FIG. 192.  $\text{Fe(CN)}^{--}$  with Thallous Acetate. 200 $\times$ .

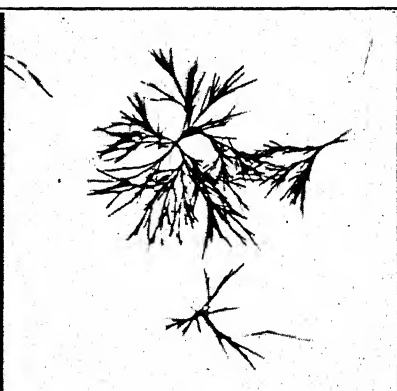


FIG. 193.  $\text{SCN}^-$  with Chloroauric Acid. 50 $\times$ .

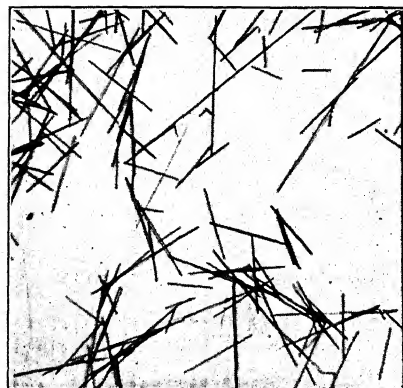


FIG. 194.  $\text{NO}_2^-$  with Silver Nitrate. 100 $\times$ .

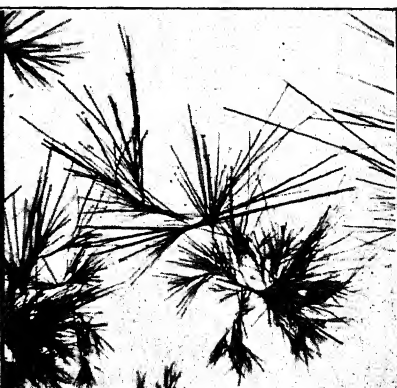


FIG. 195.  $\text{NO}_3^-$  with Nitron Sulphate. 100 $\times$ .

are decomposed by water and an insoluble basic nitrate is produced (e.g.,  $\text{BiONO}_3$ ,  $\text{SbONO}_3$ ).

Many nitrates are less soluble in  $\text{HNO}_3$  than in pure water; the most striking of these are the nitrates of  $\text{Cd}^{++}$ ,  $\text{Pb}^{++}$ ,  $\text{Sr}^{++}$ , and  $\text{Ba}^{++}$ . The latter is practically insoluble in concentrated  $\text{HNO}_3$ .

(a) *Group Reactions.*

1. No precipitate, and no separation of crystals on standing, with  $\text{AgNO}_3$ ,  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ ,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , or  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ .

(b) *With Nitron.*

Nitron sulphate<sup>1</sup> in acetic acid solution gives at once a heavy white precipitate (brown by transmitted light) consisting of sheaves of long, very slender needles and imperfect radiates (Fig. 195, page 325). The acicular crystals may develop into lath-shaped prisms exhibiting parallel extinction and moderate birefringence, but these prismatic forms are of less diagnostic value than the sheaves of needles.

The test drop must be dilute because nitron nitrate is difficultly soluble.

In very dilute solutions none of the addition products with common anions are immediately precipitated, save iodide and bichromate; but on gentle warming, the compounds formed by iodide and bichromate dissolve at once, whereas the nitrate is difficultly soluble even in warm water.

From concentrated solutions there may be obtained under favorable conditions precipitates with nitrites, chlorates, perchlorates, phosphates, chromates, bichromates, iodides, ferro- and ferri-cyanides, oxalates and tartrates; dithionates, trithionates, and pentathionates; but in no case, in dilute solutions with gentle warming, should there be any difficulty in differentiating between such precipitates and the crystals obtained with nitrates.

(c) *Reduction to  $\text{NH}_3$ .*

Nitrates are reduced to  $\text{NH}_3$  by metallic aluminum in  $\text{NaOH}$  solution. The test is performed in the apparatus shown in Fig. 10, page 17. The solution to be tested is made strongly alkaline with  $\text{NaOH}$  and several small fragments of aluminum are introduced. The crucible is covered with an object slide carrying a hanging drop of  $\text{H}_2\text{PtCl}_6$  and set aside for 30 minutes or more. If  $\text{NH}_3$  has been formed, characteristic crystals of  $(\text{NH}_4)_2\text{PtCl}_6$  will be obtained. (See page 65.)

It is, of course, essential to perform a "blank" upon the reagents and also to test the "unknown" for  $\text{NH}_3$  before the reduction with alumi-

<sup>1</sup> "Nitron" is the usual name given to Diphenylendanioldihydrotriazol. The compounds formed are direct addition products.

num is attempted. If  $\text{NH}_3$  is found in the "unknown," boil the solution with  $\text{NaOH}$  until all the  $\text{NH}_3$  has been driven off.

**Nitrites** —  $\text{NO}_2^-$ . — Most simple nitrites are water-soluble, but many double and triple nitrites are difficultly soluble or almost insoluble.

The  $\text{NO}_2^-$  ion also enters into combinations with certain of the heavy metals to form complex ions, whose true nature is still uncertain and whose detection by ordinary qualitative methods is a matter of great difficulty.

(a) *Group Reactions.*

1. With  $\text{AgNO}_3$  there is obtained a felted mass of fine needles with long acicular prisms at the outer edge of the mass; on standing, short stout prisms with imperfectly developed ends are formed (Fig. 194, page 325). These crystals are colorless under the microscope, and do not show their greenish tint unless viewed in masses by reflected light.

2. With  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  or  $\text{BaCl}_2$  no separation of crystals is obtained since  $\text{Ba}(\text{NO}_2)_2$  is readily soluble.

(b) *Oxidizing Action.*

Add to the drop to be tested a crystal of potassium iodide, then a little potato or canna starch, and finally a trace of dilute acetic acid. The hydriodic acid set free by the acid is oxidized by the nitrous acid; iodine is liberated and stains the starch blue or violet or black. This reaction is not specific as it is only the oxidizing power of  $\text{NO}_2^-$  which is tested.

Always test the potassium iodide, with starch and dilute sulphuric acid, so as to ascertain its purity and to be certain that no appreciable bluing of the starch takes place with the reagents alone.

(c) *Triple Nitrite.*

To the drop of the solution to be tested add  $\text{KC}_2\text{H}_3\text{O}_2$ , and flow into the test drop thus prepared a drop of a solution of  $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$  acidified with acetic acid. Minute crystals of potassium cobaltinitrite are obtained. (See Cobalt, page 270.)

A more satisfactory test can be made by adapting the triple nitrite reaction to the detection of  $\text{NO}_2^-$ . (See page 207.) To the test drop add  $\text{K}(\text{C}_2\text{H}_3\text{O}_2)$ ,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , and  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ , and finally  $\text{HC}_2\text{H}_3\text{O}_2$ ; tiny black cubes are obtained. (See Lead, page 207; Fig. 139, page 205.) The triple nitrite reaction is seldom applicable since with the introduction of both lead and copper there are likely to be many possible interferences.

**Cyanates** —  $\text{CNO}^-$ . — The cyanates of the alkalis are readily soluble in water; those of the alkaline earths are somewhat difficultly soluble. The cyanates of most of the remaining elements are insoluble, or only sparingly soluble.

(a) *Group Reactions.*

1.  $\text{AgNO}_3$  produces at once, even in very dilute solutions, a dense white "amorphous" precipitate. On standing a fringe of fine needles forms on the outer edge of the amorphous mass. Toward the center of the dense precipitate the acicular crystals become short and more rod-like, but well-developed prisms are seldom obtained. Although  $\text{AgCNO}$  is slightly more soluble in hot than in cold water, flowing the warm reagent into a hot test drop, or attempting to recrystallize from hot water, does not give crystals sufficiently better formed to warrant the extra trouble.

2. The addition of  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  causes the separation of colorless, tiny disks, sphero-crystals, and dumb-bell and hour-glass clusters of excessively fine needles. These crystal aggregates remain small; even on long standing a magnification of 150 to 200 $\times$  is required to disclose their habit.

3.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives an amorphous precipitate or one consisting of tiny disks somewhat irregular in outline.

4. No precipitate and no separation of crystals is obtained with  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ .

(b) *Reaction with Hydroxylamine Hydrochloride and Ferric Chloride.*

To the moderately concentrated test drop acidified with  $\text{HCl}$  add a fragment of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  about this size ( $^\circ$ ). Stir until dissolved. Flow in by Method I a dilute solution of  $\text{FeCl}_3$ . A purple-blue color results and an amorphous, deep blue precipitate is formed.

The ferric chloride solution should be of such concentration that the drop on the object slide is just distinctly yellow when viewed over a white background.

The best results are obtained when the test drop is approximately neutral or very slightly acid with  $\text{HCl}$ .

$\text{CNO}^-$ , if in alkaline solution, gives a precipitate of hydrous ferric oxide, and, if then acidified with  $\text{HCl}$ , no visible reaction is obtained; but on long standing a precipitate of Prussian blue separates.  $\text{CN}^-$  gives the Prussian blue reaction at once, in acid solution.

Fossé<sup>2</sup> has shown that this test can be applied to a precipitate of  $\text{AgCNO}$  which has been obtained with  $\text{AgNO}_3$ . The supernatant liquor is decanted and the precipitate washed thoroughly. A large fragment of hydroxylamine hydrochloride is added and the preparation stirred until the reagent is dissolved. A drop of  $\text{FeCl}_3$  solution is added as above. A blue or violet color is produced.

Soluble alkali cyanates treated with  $\text{FeCl}_3$  and then with dilute  $\text{HCl}$

<sup>2</sup> *Compt. rend.* 171, 722 (1920).

give a blue color and a blue precipitate of Prussian blue, but the color first formed when hydroxylamine is present is of a different hue and of greater intensity.

When the concentration of  $\text{CNO}^-$  ions in the test drop is high, the purple or red-violet color first produced may change to a reddish brown and a brown precipitate may be formed. Under such conditions add to the center of the brown mass a tiny drop of dilute  $\text{HCl}$ . The hydrous oxide of iron is dissolved, and a precipitate of Prussian blue is brought into evidence.

(c) *Reaction with Cobalt Acetate.*

To the *concentrated* test drop add at its center a fragment of  $\text{KC}_2\text{H}_3\text{O}_2$  and a *tiny* crystal of  $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$ . The crystal will be surrounded immediately by a deep blue zone of color, in which floats a dark-colored "amorphous" precipitate. As the reagent dissolves, the blue zone increases in diameter and eventually reaches the circumference of the drop. Allow the preparation to stand and spontaneously evaporate to dryness. Tablets, prisms, and large coarse dendrites of the deep blue ("cobalt blue") tetragonal salt  $2\text{KCNO} \cdot \text{Co}(\text{CNO})_2$  are obtained. The test is successful only when  $\text{CNO}^-$  ions are in excess of  $\text{Co}^{++}$  and a double salt is possible. It is therefore imperative that the  $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$  be added with great caution; otherwise merely a fugitive blue color will be obtained and no blue salt will be found as the test drop passes to dryness.

The ion  $\text{SCN}^-$  also yields a blue color and a blue salt with cobalt acetate, but the hue of blue is very different and the dendrites of the cobalt thiocyanate salt have a different habit. A blue thiocyanate can be obtained only when the test drop consists of a practically saturated solution of an alkali thiocyanate.

Differentiation is simple if the blue color obtained with the unknown is compared with that given by drops prepared with  $\text{KCNO}$  and  $\text{KSCN}$ .

Another excellent method of distinguishing between the blue of  $\text{CNO}^-$  and that of  $\text{SCN}^-$  is to add a small drop of isoamyl alcohol to the preparation before it passes to dryness, stirring so as to bring the drop of the alcohol into intimate contact with all parts of the test drop. The blue cobalt cyanate salt is insoluble in the alcohol, but the thiocyanate salt is readily soluble; and in the latter case the drop of isoamylalcohol turns deep blue.<sup>3</sup>

Alkali cyanides yield no blue compound. If the cyanate contains even a small amount of cyanide, the formation of the blue zone is pre-

<sup>3</sup> Fossé: *Compt. rend.* 171, 722 (1920).

vented, and as the fragment of  $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$  dissolves it will be surrounded by a yellow or brown zone.

(d) *Detection of  $\text{CNO}^-$  based upon its decomposition products,  $\text{CO}_2$  and  $\text{NH}_3$ .*

When an alkali cyanate is heated with dilute  $\text{H}_2\text{SO}_4$ ,  $\text{CO}_2$  is given off and  $(\text{NH}_4)_2\text{SO}_4$  is formed in the solution.

Place the material in the crucible of the distilling apparatus (Fig. 10, page 17), proceeding as described on page 41. Add two or three drops of dilute  $\text{H}_2\text{SO}_4$ , cover with an object slide carrying a hanging drop of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ . Warm gently. Remove the slide and examine the drop for crystals of lead carbonate. Evaporate the solution almost to dryness in the crucible, cool, add  $\text{NaOH}$ , and cover with a slide having a hanging drop of  $\text{H}_2\text{PtCl}_6$ . Search for crystals of  $(\text{NH}_4)_2\text{PtCl}_6$ .

A "blank" must be made upon unknown and reagents to ensure the absence of  $\text{NH}_3$ .

If the unknown contains  $\text{NH}_4\text{CNO}$ , it is obvious that the test for  $\text{NH}_3$  production can give no evidence of the presence of  $\text{CNO}^-$  ions.

**Cyanides —  $\text{CN}^-$ .**—The alkali salts of the ion  $\text{CN}^-$  are very readily soluble in water, as are also the calcium and the strontium salts, but the barium salt is only slightly soluble. The cyanides formed by the remaining common elements are practically insoluble with the exception of  $\text{HgCN}$ , which is slightly soluble.

However, many of these insoluble cyanides unite with the cyanides of the alkalis to form double salts which are readily soluble in water.

An aqueous solution can therefore contain both simple and double cyanides and also a number of complex cyanides.

Cyanogen enters into combinations to form a third class of compounds in which it constitutes a part of a complex ion—as, for example, in  $\text{K}_4\text{Fe}(\text{CN})_6$  and  $\text{K}_3\text{Fe}(\text{CN})_6$ , the anions in these cases being the complexes  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Fe}(\text{CN})_6^{3-}$ . Besides ferrous and ferric iron in these complexes we also find salts of  $\text{Mn}(\text{CN})_6^{4-}$ ,  $\text{Cr}(\text{CN})_6^{3-}$ ,  $\text{Co}(\text{CN})_6^{3-}$ ; other complex ions are formed with members of the platinum group. Some of the salts of these complex anions are water-soluble, some are insoluble.

The simple cyanides and double cyanides are readily transformed by acids into salts of the acid used and  $\text{HCN}$  is set free, with possibly  $\text{C}_2\text{N}_2$ . But in the case of the complexes the addition of the acid has no appreciable effect, save that in certain complexes boiling with strong acids in concentrated solution may bring about a decomposition of the complex with the liberation of part if not all the cyanogen as  $\text{HCN}$ .



In these complex ions neither the metal nor the cyanogen responds to identity tests for the simple cations or anions corresponding to them unless the complex is broken down.

(a) *Group Reactions.*

1.  $\text{AgNO}_3$  gives a heavy white, curdy precipitate. In very dilute solutions exceedingly minute prismatic crystals are obtained provided a *slight excess* of  $\text{AgNO}_3$  is used, but a decided excess must be avoided.  $\text{AgCN}$  forms a number of water-soluble double cyanides; a precipitate first formed may therefore redissolve.

2.  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  added to solutions containing alkali cyanides gives a turbidity or precipitate consisting of tiny colorless dendritic aggregates, resembling clumps of moss.

(b) *Detection by Evolution of HCN.*

For this purpose we can use the distilling crucible, proceeding as outlined on page 41. The material in question is moistened with several drops of dilute  $\text{H}_2\text{SO}_4$  and covered with an object slide carrying a hanging drop of  $\text{AgNO}_3$ . Warm very gently and set aside for a few minutes. The drop of  $\text{AgNO}_3$  is then searched for crystals of  $\text{AgCN}$ . These are very tiny, highly refractive, short, stout prisms or rods, or sheaves of very slender needles (Fig. 191, page 325). A magnification of 150 to 200 $\times$  is required for their resolution. If colorless crystals are found to have been formed, carefully acidify the preparation with dilute  $\text{HNO}_3$ ;  $\text{AgCN}$  is insoluble, but  $\text{Ag}(\text{CN})_2$  is readily soluble.

If no precipitate, turbidity, or cloudiness is formed in the drop of  $\text{AgNO}_3$ , it is safe to conclude that no  $\text{HCN}$  has been formed by the action of the  $\text{H}_2\text{SO}_4$ . The formation of  $\text{AgCN}$  cannot be taken as proof of the presence of  $\text{CN}^-$  ions, for the  $\text{H}_2\text{SO}_4$  may have caused the liberation of  $\text{HCN}$  by decomposition of certain complex ions such as  $\text{FeCN}_6^{4-}$ , etc. If, therefore, crystals of  $\text{AgCN}$  have been found, the experiment is repeated, using this time  $\text{HNaCO}_3$  instead of  $\text{H}_2\text{SO}_4$ . Under these conditions crystals of  $\text{AgCN}$  will be formed from  $\text{CN}^-$  liberated from easily decomposable cyanides, but not from the more stable complex ions, nor from stable cyanides not decomposable by  $\text{HNaCO}_3$ .

Instead of  $\text{AgNO}_3$  in the hanging drop, a drop of  $(\text{NH}_4)_2\text{S}$  can be used to absorb the  $\text{HCN}$  set free. Careful evaporation of the reagent drop to dryness will give  $\text{NH}_4\text{SCN}$ , which can be tested for by  $\text{FeCl}_3$  (formation of blood-red  $\text{Fe}(\text{SCN})_3$ ).

Or the absorption can be made in a drop of a solution of sodium picrate with the production of a deep red color (picrocyanate,  $\text{NaC}_8\text{H}_4\text{N}_5\text{O}_6$ ). This reaction is of value when thus performed, but is not specific for  $\text{CN}^-$  if the reagent is applied directly to test drops, for

a number of reducing substances give a red color with picric acid or sodium picrate.

**Thiocyanates ( $\text{SCN}^-$ ).**—The thiocyanates of the alkalis, alkaline earths, and  $\text{Fe}^{+++}$  are readily soluble in water. Those of  $\text{Mn}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Co}^{++}$  are also water-soluble but less readily; those of  $\text{Cu}^{++}$  and  $\text{Hg}^{++}$  are sparingly soluble; those of the other metals are insoluble or difficultly soluble.

Many double and triple thiocyanates are formed having variable solubilities in water; in some cases the double salts are more soluble than either of the combining simple thiocyanates; in other cases the double thiocyanates are less soluble.

(a) *Group Reactions.*

1.  $\text{AgNO}_3$  produces an instantaneous, heavy white, curdy precipitate, soluble in excess of potassium thiocyanate but insoluble in excess of ammonium thiocyanate and insoluble in dilute nitric acid.

2. With  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  no precipitate and no separation of crystals is obtained.

3. With  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  there is no apparent reaction.

4.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  yields a precipitate in which no evidence of crystals can be detected, but merely a granular or sandy appearance with no change on standing.

5.  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$  produces at once a mass of fine needles and irregular acicular dendrites. On standing, elongated, symmetrical, six-sided plates and tablets are formed, also long thin plates with oblique ends. Hexagonal skeletons are also abundant, and imperfectly developed plates and prisms. These crystals are strongly birefringent, and exhibit very brilliant polarization colors.

6. To the test drop add a very little  $\text{HgCl}_2$ ; stir until dissolved, then flow in by Method I a dilute solution of  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ . In the presence of  $\text{SCN}^-$  the double thiocyanate of  $\text{Hg}^{++}$  and  $\text{Zn}^{++}$  will be formed. (See pages 136–144, Fig. 96, page 139.) The addition of a trace of cobalt or of copper will color the crystals of the double salt, and thus increase the sensitivity of the reaction.

7. Flow into the test drop a very dilute solution of  $\text{FeCl}_3$ . A blood-red or yellowish-red color results from the formation of soluble ferric thiocyanate.

**Complex Cyanides.**—Cyanogen enters into many combinations which function as complex ions. Some of these complicated compounds are of debatable structure and are especially prevalent in the eighth group of the Periodic System. Of these complex ions,  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Fe}(\text{CN})_6^{3-}$  are the only ones which are commonly encountered in industrial analyses.

**Ferrocyanides** —  $\text{Fe}(\text{CN})_6^{4-}$ . — The alkali ferrocyanides are readily soluble in water and form easily crystallizable salts.

The ferrocyanides of the alkaline earths are also soluble in water but less readily than those of the alkalis.  $\text{Mg}_2\text{Fe}(\text{CN})_6$  is also water-soluble.

With the alkali ferrocyanides, many other ferrocyanides form double salts whose solubilities are different from those which might be expected. For example, the potassium calcium ferrocyanide is less soluble than calcium ferrocyanide, whereas the potassium barium ferrocyanide is more soluble than barium ferrocyanide. Analogous phenomena are to be met with in double salts of other elements.

The ferrocyanides of most of the elements other than the alkalis and alkaline earths form salts insoluble or difficultly soluble in water and must be boiled with a solution of sodium carbonate, the solution filtered, carefully neutralized with dilute  $\text{HCl}$  or  $\text{HNO}_3$ , and concentrated if necessary before any dependable tests may be obtained.

The great majority of ferrocyanides give almost colorless solutions in test drops, and small thin crystals, and most precipitates appear colorless or white. The most striking exceptions are those of iron, copper, and uranium.

(a) *Group Reactions.*

1.  $\text{AgNO}_3$  yields at once, even in very dilute solutions, a white, heavy, gelatinous precipitate of uniform texture throughout. There is no perceptible change in the "amorphous" character of the precipitate as the test drop passes to dryness.

2. With  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  no separation of crystals of  $\text{Ba}_2[\text{Fe}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$  takes place unless the test drop is very concentrated. (See Barium, page 123.) If the concentration is sufficiently high, or the drop passes to dryness, colorless, weakly birefringent monoclinic, nearly rectangular tablets are obtained (Fig. 69, page 105). With  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  there is obtained, on standing for some seconds, a fine granular precipitate which slowly changes into very minute square and rectangular plates and tablets (Fig. 68, page 105).

3.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  precipitates in very dilute solutions a white granular salt, which soon becomes distinctly crystalline. The tiny crystals present a great variety of shapes; there are irregular, rounded and angular grains, dendritic aggregates, tiny rods and rectangular prisms, some exhibiting parallel and some oblique extinction. All are strongly birefringent.

4. With  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$  there is first obtained a white or colorless precipitate of tiny crystalline, very irregular grains; these develop into elongated, somewhat dendritic, six-sided plates, and thin plates in the

form of regular hexagons. The plates are highly refractive, strongly birefringent, and exhibit brilliant polarization colors.

(b) *Prussian Blue.*

$\text{Fe}(\text{CN})_6^{4-}$  gives a dark blue flocculent precipitate with both  $\text{Fe}^{++}$  and  $\text{Fe}^{+++}$ , insoluble in  $\text{HCl}$ . With  $\text{Cu}^{++}$  a chocolate-brown, curdy or flocculent precipitate is obtained.

(c) Benzidine hydrochloride, added by Method I, does *not* give a blue oxidation product (distinction from  $\text{Fe}(\text{CN})_6^{3-}$ ), for  $\text{Fe}(\text{CN})_6^{4-}$  acts as a reducing compound, the iron in the complex being in the ferrous condition.

(d) *Reaction with Quinoline.*

Quinoline hydrochloride gives rise to the formation of a difficultly soluble, double quinoline ferrocyanide, separating in brownish-yellow or brown, strongly birefringent, tablets and thin plates. A few tablets elongate and become prismatic. The tablets are almost square or rectangular in outline, but many rhombiform tablets and grains are to be found with very acute angles. The crystals are dichroic and exhibit oblique extinction.

A moderate concentration of the test drop yields the best results. Free acids must be absent; their deleterious action can be mitigated by adding an alkali acetate.

**Ferricyanides**— $\text{Fe}(\text{CN})_6^{3-}$ .—The ferricyanides of the alkalis and alkaline earths are readily soluble in water. Many of the other elements give insoluble or sparingly soluble salts, but under the normal conditions which obtain in microscopical qualitative analysis no precipitate is probable with  $\text{Al}^{+++}$ ,  $\text{Hg}^{++}$ ,  $\text{Pb}^{++}$ ,  $\text{Sb}^{+++}$ ,  $\text{Sn}^{++++}$ ,  $\text{Cr}^{+++}$ ,  $(\text{UO}_2)^{++}$ ,  $\text{Fe}^{+++}$ . Insoluble ferricyanides may be converted into soluble alkali ferricyanides by heating with a solution of sodium carbonate.

The ferricyanides commonly met with are reddish in color and give reddish-colored solutions.

A number of salts of  $\text{Fe}(\text{CN})_6^{3-}$  are soluble in 95 per cent alcohol; the corresponding salts of  $\text{Fe}(\text{CN})_6^{4-}$  are not.

(a) *Group Reactions.*

1. With  $\text{AgNO}_3$  there is formed a heavy, reddish-brown, gelatinous precipitate, which undergoes no change in its physical appearance as the test drop passes to dryness.

2. With  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  no precipitate is obtained, and no separation of crystals until the test drop has evaporated to dryness. In the crystalline mass which results, it is impracticable to identify crystals of  $\text{Ba}_3[\text{Fe}(\text{CN})_6]_2$  which may have been formed.

3.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives results analogous in all respects to those obtained with  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ .

4. With  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$  no precipitate is obtained and, on standing, no crystals ordinarily separate; but, as the test drop concentrates by spontaneous evaporation, there appears around the circumference a crystalline crust in which can be seen yellow and reddish-brown dendrites. If these dendrites are crushed so as to "seed" the preparation, short, stout, bipyramidal prisms and irregular crystalline grains are obtained. These crystals of thallium ferricyanide are remarkably dichroic. If thin, the change is from yellow to reddish-brown; if thick, from reddish-brown to jet black. They are strongly birefringent and extinguish parallel to the direction of elongation.

When testing for  $\text{Fe}(\text{CN})_6^{--}$  it is essential that the test drop, to which  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$  has been added, shall be allowed to stand until it becomes almost supersaturated, and then seeded.

(b) *Prussian Blue.*

$\text{Fe}(\text{CN})_6^{--}$  gives a dark blue precipitate (or solution) with ferrous salts *but not with ferric salts* (distinction from  $\text{Fe}(\text{CN})_6^{---}$ ). With solutions containing  $\text{Fe}^{+++}$  no perceptible change in the test drop can be observed, unless both test drop and reagent are concentrated; under these latter circumstances a brown color is developed.

(c) *Oxidizing Action.*

Benzidine hydrochloride<sup>4</sup> added by Method I yields blue prisms, stars, and irregular dendrites and grains. This reaction is due to the oxidizing power of  $\text{Fe}(\text{CN})_6^{--}$  and is not specific for this ion. Any mild oxidizing agent under similar conditions will give a similar reaction. Nevertheless the reaction is frequently useful in differentiating between ferro- and ferric-cyanides.

(d) *Reaction with Quinoline.*

Quinoline hydrochloride, added as in testing for  $\text{Fe}(\text{CN})_6^{---}$ , gives a bright yellow precipitate consisting of large prismatic dendrites. These crystals are rough and almost opaque at first, but some of them may become clear and transparent on standing. Many-faced, lemon-yellow tablets also appear after a short time; were it not for their color, these tablets might be confused with those given by  $\text{Fe}(\text{CN})_6^{--}$ . They are, however, less birefringent and are not noticeably dichroic. Extinction is oblique.

<sup>4</sup> Behrens: *Zeit. anal. Chem.* 43, 423 (1904).

## DETECTION OF THE ANIONS OF THE PHOSPHORUS GROUP

$(\text{H}_2\text{PO}_2)^-; (\text{HPO}_3)^{--?}; (\text{PO}_3)^-; (\text{PO}_3)^{\text{---}}; (\text{P}_2\text{O}_7)^{\text{---}}; (\text{P}_4\text{O}_{13})^{\text{---}};$   
 $(\text{PO}_4)^{\text{---}}; (\text{P}_2\text{O}_6)^{\text{---}}?; (\text{AsO}_2)^-; (\text{AsO}_3)^{\text{---}}; (\text{AsO}_4)^{\text{---}}; (\text{As}_2\text{O}_7)^{\text{---}}$

No group of inorganic anions included in this Handbook gives rise to the formation of such a multiplicity of complex acids and salts as does the Phosphorus Group of Anions.

This great group includes anions and salts to which definite formulas have been ascribed but whose existence is doubtful. This has led to the description, at different times, under different names, of the same anion and its reactions. The data available in the literature are incomplete and contradictory, and in many instances appear to have been obtained upon material of very doubtful purity.

Recent years have witnessed an ever-increasing number of exceedingly complex acids of phosphorus whose existence is claimed and some of whose salts have been described, but for which there are no known qualitative reactions.<sup>5</sup> The problem before the analyst is, therefore, a most difficult one, for the increased use in the industries of complex alkali phosphates as precipitants, water softeners, detergents, etc., has required the recognition of the type of phosphatic material in question. The problem is further complicated by the introduction of salts other than phosphates to prevent "caking" (fluorides, intumescend borax, and other compounds). These additions not only interfere with or change the reactions of the phosphate anions toward reagents, but may cause profound changes in the crystallographic and optical character of the phosphatic salt. A striking example of this is to be found in trisodium phosphate— $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$ —which, when pure, is trigonal, whereas the commercial detergent containing less than one per cent F exhibits a large proportion of  $2 \text{Na}_3\text{PO}_4 \cdot \text{NaF} \cdot 19 \text{H}_2\text{O}$ , an isometric compound.<sup>6</sup>

**Orthophosphates** —  $\text{PO}_4^{\text{---}}$ . — The mono-, di-, and tri-alkali phosphates are well known. All are soluble in cold water.

Some of the mono (acid) phosphates of the alkaline earths are water soluble.

With the exception of those of the alkalis, substantially all normal and acid orthophosphates are insoluble.

Solutions of the di- and tri-alkali phosphates precipitate solutions of nearly all other salts. The precipitate consists of a di- or tri-metal orthophosphate or a basic phosphate.

<sup>5</sup> See Britzinger and Ratanarat: *Zeit. anorg. allgem. Chem.* 228, 61 (1936); Durgin, Lum, and Malowan: *Trans. Amer. Inst. Chem. Eng.* 33, 643 (1937).

<sup>6</sup> Mason and Ashcraft: *Ind. Eng. Chem.* 31, 768 (1939).

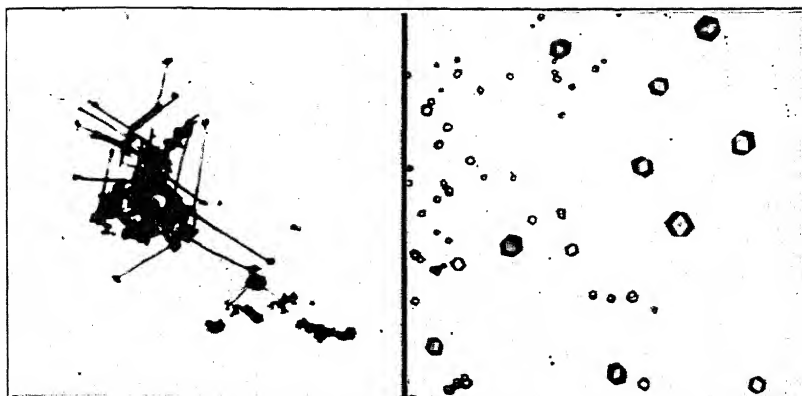


FIG. 196.  $\text{AsO}_4^{---}$  with Silver Nitrate. 500 $\times$ .

FIG. 197.  $\text{AsO}_4^{---}$  with Silver Nitrate. 500 $\times$ .

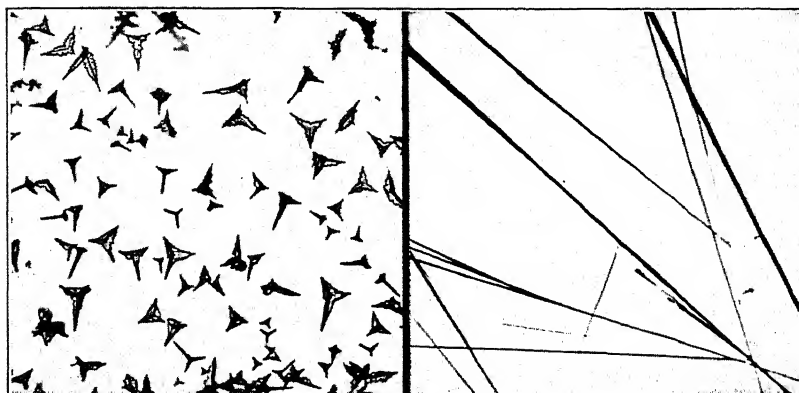


FIG. 198.  $\text{PO}_4^{---}$  with Silver Nitrate. 200 $\times$ .

FIG. 199.  $\text{PO}_4^{---}$  with Thallous Acetate. 50 $\times$ .



FIG. 200.  $\text{HPO}_3^{--}$  with Calcium Acetate. 150 $\times$ .

FIG. 201.  $\text{HPO}_3^{--}$  with Barium Acetate. 300 $\times$ .

All orthophosphates are dissolved or transposed by  $\text{HNO}_3$ ,  $\text{HCl}$ , or  $\text{H}_2\text{SO}_4$ . Nearly all are dissolved by  $\text{HC}_2\text{H}_3\text{O}_2$ ; the common exceptions are  $\text{Pb}^{++}$ ,  $\text{Al}^{+++}$ ,  $\text{Fe}^{+++}$ . Nearly all are dissolved by  $\text{H}_3\text{PO}_4$ ; the exceptions are  $\text{Hg}^{++}$ ,  $\text{Pb}^{++}$ ,  $\text{Sn}^{--}$ ,  $\text{Bi}^{+++}$ .

Commercial orthophosphoric acid consists of a mixture of orthophosphoric, pyrophosphoric, metaphosphoric, and probably some polyphosphoric acid. Commercial orthophosphates are therefore likely to be mixtures. Most of them are likely to contain fluorides.

(a) *Group Reactions.*

1.  $\text{AgNO}_3$  produces at once a heavy *light yellow* "amorphous" precipitate. (See Silver Group, page 317.) The precipitate soon becomes granular, and, in a zone just beyond the precipitate, tiny, yellow dendritic stars, crosses, radiates, and irregular clusters of fine needles are formed. Crystals which float are especially characteristic; most of them are three-branched (Fig. 198, page 337), more or less feathery or rough dendrites; the ends of each of the three branches are forked. As the concentration rises through spontaneous evaporation, tiny, highly refractive, yellow, crystalline triangular and tetrahedral grains separate around the circumference of the test drop.

2. With  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  and with  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  a heavy, white, "amorphous" precipitate is obtained which may become granular on standing; but no recognizable crystals are formed.

3.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  throws down a heavy, white, curdy precipitate. On standing, very minute rods and needles appear. They occur singly in crosses, X's, and very small radiates. A magnification of about  $300\times$  is required to reveal their form.

4. With  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$  a very characteristic reaction is obtained. When the reagent is first added no result follows, but, on standing, very long, colorless, slender needles appear in large, loose, radiating clusters and in wisps. When the concentrations are favorable the needles grow so long as to extend completely across the field of view. (See  $\text{CO}_3^{--}$ , page 324, Fig. 199, page 337, Fig. 190, page 325.)

(b) *Reaction with "Magnesia Mixture."*

In a drop of water dissolve a little  $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$ , add about twice as much  $\text{NH}_4\text{Cl}$ , stir and add a drop of  $\text{NH}_4\text{OH}$ . Into this reagent drop introduce a fragment of the material to be tested, and warm very gently. With orthophosphates  $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$  separates in large colorless feathery dendritic stars and skeleton crystals. See also Ammonium, page 76; Magnesium, page 130, Figs. 76, 77, page 109.  $(\text{H}_2\text{PO}_2)^-$  gives no precipitate and no separation of crystals;  $(\text{HPO}_3)^-$  yields tiny, six-pointed stars and rosettes, curious dendrites reminding one of butterflies, and elongated plates with parallel sides and irregularly acute



ends.  $\text{PO}_3^-$  gives an "amorphous" precipitate, then a few curious dendritic crystals.  $\text{P}_2\text{O}_7^{4-}$  yields a gelatinous precipitate only.

$\text{AsO}_4^{3-}$  gives a reaction identical with that of  $\text{PO}_4^{3-}$ ; the reaction products are isomorphous. To differentiate between the crystalline precipitates formed by these two anions, wash the precipitate with dilute  $\text{NH}_4\text{OH}$ , dissolve in very little acetic acid, and apply to a drop of the solution silver nitrate by Method I. Arsenates yield dark red crystals, phosphates a yellow precipitate. Interpretation of results is likely to be difficult in mixtures of arsenates and phosphates.

(c) *Reaction with Ammonium Molybdate.*<sup>7</sup>

Upon an object slide place a large drop of an almost saturated solution of ammonium molybdate acidulated with nitric acid. Adjacent to this drop place a concentrated solution of the material to be tested. This test drop must be an aqueous solution and neutral or nearly so. Cause the test drop to flow into the reagent drop. Do not warm. Examine the preparation at once. Orthophosphates yield immediately a lemon-yellow precipitate of ammonium phosphomolybdate in the form of minute granules developing into highly refractive, isotropic disks, spheres, octahedra, and sometimes cubes.

The preparation should be studied directly after the drops are united, because all (?) the other phosphorus anions, on standing for a short time, may become transformed in part into orthophosphates: owing to this instability, the test drop should be that of a freshly prepared solution.

Warming in the presence of nitric acid greatly accelerates transformations and destroys the diagnostic value of the test.

Performed at room temperatures in the manner suggested, the reaction appears to be characteristic of  $\text{PO}_4^{3-}$ . None of the alkali salts of the other phosphorus anions which have been tested by the writers yield a voluminous yellow precipitate in less than one minute. As, Si, W, V, Al must be absent.

Since the transformation of anions giving no immediate precipitate with ammonium molybdate into anions reacting at once with this reagent is always slow at room temperature, an experienced analyst by working rapidly runs little risk of misinterpreting reactions. The problem is not so simple when a small percentage of  $\text{PO}_4^{3-}$  exists in salts other than orthophosphates, for it then becomes a question

<sup>7</sup> Samples of ammonium molybdate, C.P., made by different firms appear to be somewhat variable in composition.

For sensitive, microscopical qualitative reactions it is advisable to recrystallize the commercial product once or twice from hot distilled water and employ fragments from clear, well-formed crystals.

whether the  $\text{PO}_4^{---}$  has been produced by the action of the  $\text{HNO}_3$ . To solve such problems tests must be made for all of the phosphorus group ions, and from the data thus obtained a reliable decision can usually be reached.

Under the conditions given above for the performance of the test, metaphosphates —  $\text{PO}_3^-$  — appear to be far more rapidly converted into orthophosphates —  $\text{PO}_4^{---}$  — than the other salts listed in the preceding paragraph. Ammonium molybdate cannot therefore be depended upon to differentiate between  $\text{PO}_3^-$  and  $\text{PO}_4^{---}$ .

**Metaphosphates —  $\text{PO}_3^-$ .** — The acid  $\text{HPO}_3$  is monobasic but is prone to polymerizing, giving acids of the general formula  $(\text{HPO}_3)_n$ . The sodium salts of two of the many possible polymers are well-known  $(\text{NaPO}_3)_4$  and  $(\text{NaPO}_3)_6$ . Most metaphosphates are difficultly soluble or insoluble in cold water. They are not stable in solution but undergo changes not yet fully understood, save that one of the products is believed to be always an orthophosphate; heat speeds the transformation.

The metaphosphates likely to be met with in dealing with commercial products are the normal sodium metaphosphate —  $\text{NaPO}_3$ ; sodium hexametaphosphate —  $\text{Na}_6\text{P}_6\text{O}_{18}$ , i.e.,  $(\text{NaPO}_3)_6$ ; and the sodium salt of the acid  $\text{H}_6\text{P}_4\text{O}_{13}$ , sodium tetrphosphate. The last is probably not a mixture of a metaphosphate polymer plus some other phosphatic salt, but because of its similar microanalytical behavior it is convenient to group it with the metaphosphates.

All the polymerized metaphosphates manufactured on a large scale appear to be mixtures and to contain pyrophosphates.<sup>8</sup>

### *Group Reactions.*

1.  $\text{AgNO}_3$  produces a white "amorphous" or sometimes granular precipitate. It is seldom that a test drop yields crystals of  $\text{AgPO}_3$ . In rare cases tiny dendritic aggregates are obtained, in the form of lichen-like clumps, or rosettes of peculiar form.  $\text{AgPO}_3$  is soluble in  $\text{NH}_4\text{OH}$ .

2. Neither  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ ,  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ ,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , nor  $\text{Ti}(\text{C}_2\text{H}_3\text{O}_2)_2$  yields results other than slight "amorphous" or granular precipitates.

3. To a drop of "magnesia mixture" (see  $\text{PO}_4^{---}$ , page 338) add a fragment of the material to be tested; warm *very gently*. An "amorphous" precipitate is obtained, with here and there a few curious dendrites of indescribable form, derived from fusiform rods or elliptical

<sup>8</sup> The authors are greatly indebted to Dr. T. G. Rochow for the samples of meta-, tetra-, and pyro-phosphates upon which the reactions as described have been based; and to Dr. Rochow and R. L. Gilbert, Jr., for communications summarizing their experiences with microscopical tests for the phosphorus-containing anions.

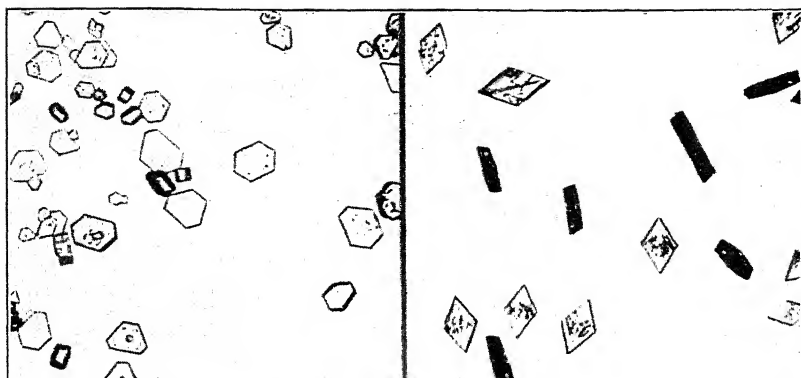


FIG. 202.  $P_2O_7^{4-}$  with Luteo-cobalt Chloride. 200 $\times$ .

FIG. 203.  $SO_4^{2-}$  with Silver Nitrate. 100 $\times$ .



FIG. 204.  $SO_4^{2-}$  with Thallous Acetate. 200 $\times$ .

FIG. 205.  $SO_4^{2-}$  with Thallous Acetate. 200 $\times$ .

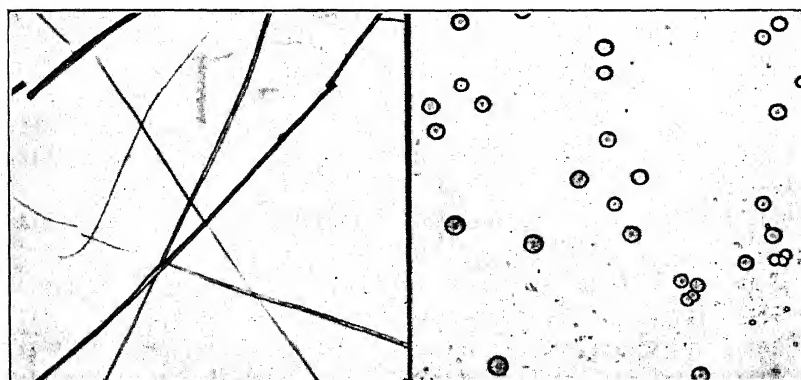


FIG. 206.  $SeO_4^{2-}$  with Thallous Acetate. 200 $\times$ .

FIG. 207.  $SO_3^{2-}$  with Calcium Acetate. 200 $\times$ .

plates. These crystals are quite different from those obtained with  $\text{PO}_4$ —.

(a) Aqueous solutions of salts of metaphosphoric acid, when added to a solution of egg albumen acidified with acetic acid so as to be just acid to litmus, cause the albumen to coagulate. Orthophosphates, pyrophosphates, cause no coagulation. Tetraphosphates do not coagulate the albumen *at this acidity*, but will cause coagulation in the presence of a greater excess of acetic acid. These are test-tube reactions and not generally obtainable on object slides.

(b) Ammonium molybdate yields no immediate precipitate. After the preparation stands for a few minutes there may be found in scattered areas faintly yellow grains and almost colorless octahedra; as the drop passes to dryness the residue is white not yellow. (See Orthophosphates, 339.)

(c) Luteocobalt chloride yields oily drops, colorless at first, turning yellow slowly. (See Pyrophosphates.)

**Pyrophosphates** —  $\text{P}_2\text{O}_7$ —.— In the acid  $\text{H}_4\text{P}_2\text{O}_7$  all four H atoms are replaceable. The salts formed are stable; those of the alkalis are soluble in water; those of the alkaline earths are difficultly soluble; most other pyrophosphates are insoluble.

$\text{P}_2\text{O}_7$ — fails to yield satisfactory crystals with the reagents usually employed.

With  $\text{AgNO}_3$  a white gelatinous precipitate is obtained, becoming granular on standing and showing under a magnification of  $300\times$  rod-like bodies and oval grains.

With barium, calcium, and lead acetates a gelatinous precipitate is obtained, in which no evidence of crystallization can be discovered with a magnification of  $300\times$ .

$\text{Ti}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives no precipitate, but as the test drop passes to dryness, small disks, hexagonal plates, and rosettes are obtained.

Ammonium molybdate gives no immediate precipitate, but on standing the  $\text{HNO}_3$  converts some of the  $\text{P}_2\text{O}_7$ — into  $\text{PO}_4$ — and a precipitate slowly develops. (See Orthophosphates, page 339; Metaphosphates, page 342.)

Solutions of egg albumen are not coagulated by pyrophosphates. (See Metaphosphates, page 342.)

Luteocobalt chloride —  $\text{CoCl}_3(\text{NH}_3)_6$  —<sup>9</sup> appears to afford the most characteristic reaction now available.

When a moderately concentrated solution of this reagent is caused to flow into a drop of a not-too-dilute solution of an alkali pyrophosphate,

<sup>9</sup> Behrens-Kley: *op. cit.*, p. 139.

there is instantly formed a thick, pasty, yellow-brown precipitate filled with curving feathery-appearing dendrites and drusy needles; thin flexible blades with irregular broken edges are also present. The gelatinous or pasty mass in which they are imbedded is isotropic but is filled with anisotropic granules. The acicular and dendritic crystals exhibit moderate birefringence. After standing a few seconds thin scales and plates appear in a zone just outside the gelatinous mass and develop into isotropic, six-sided plates and tablets (Fig. 202, page 341); skeleton rosettes and small, stout hexagonal prisms may abound. The dendritic scales, and what appear to be needles, are probably plates edgewise.

This reaction is characteristic of the pyrophosphate anion; no other anion of the phosphorus group behaves in a like manner, but the reaction is not specific for  $P_2O_7$ .

The formation of the diagnostic, six-sided plates is prevented by metaphosphates and tetraphosphates. These salts yield emulsions of colorless or yellow oily material with no evidence of crystal formation until the preparations begin to pass to dryness, when clumps of thin plates may appear and thin, birefringent, tiny disks separate within the largest oily drops. Since commercial hexametaphosphates and tetraphosphates probably always contain pyrophosphates, the most plausible explanation of the clumps of thin plates is that they are due to  $P_2O_7$  anions and separate only when the compound becomes sufficiently highly concentrated, as the test drop evaporates.

Another phenomenon for which we have as yet no suitable explanation is that in some preparations orthophosphates seriously interfere with the detection of pyrophosphates, while in others they seem to have no effect whatever.

Certain of the polythionates give crystalline precipitates with luteocobalt chloride. (See Polythionates, page 360.)

Reactions may also be obtained<sup>10</sup> with  $SO_4^{--}$ ;  $S_2O_3^{--}$ ;  $CrO_4^{--}$ ;  $Cr_2O_7^{--}$ ;  $SiF_6^{--}$ ;  $IO_3^-$ ;  $Fe(CN)_6^{--}$ ;  $Fe(CN)_6^{--}$ ;  $S_2O_8^{--}$ ;  $VO_3^-$ ;  $MnO_4^{--}$ ,  $WO_4^{--}$ .

Both  $(MoO_4^{--})?$  and  $WO_4^{--}$  give with luteocobalt chloride sheaves and radiates, and finally hexagonal scales, and plates, as the test drop goes to dryness; these crystals differ so little in appearance from those obtained with  $P_2O_7^{--}$  as to be practically indistinguishable. There is, nevertheless, little danger of error, for with  $P_2O_7^{--}$  the precipitation is instantaneous, while with  $(MoO_4^{--})?$  nothing is at first seen, and with  $WO_4^{--}$  the first reaction is a mere turbidity.

**Hypophosphates— $P_2O_6^{--}$ .**—Comparatively little is known concerning these rare salts. They are quite stable and are not readily

<sup>10</sup> Hynes: *Mikrochemie* 23, 1 (1937).

oxidized to phosphates by such energetic agents as  $\text{Cl}_2$ ,  $\text{H}_2\text{CrO}_4$  or  $\text{H}_2\text{O}_2$ .

The ion  $\text{P}_2\text{O}_6$  is tetravalent; mono-, di-, tri-, and tetra-alkali salts are known. All are water-soluble. Most of the other elements form difficultly soluble salts with  $\text{P}_2\text{O}_6$ ----

Since hypophosphates are not obtainable in commerce and are still of more theoretical than practical use, the detection of this ion need not be considered here.

**Hypophosphites** —  $(\text{H}_2\text{PO}_2)^-$ . — Hypophosphorous acid  $\text{H}_3\text{PO}_2$  is a monobasic acid, only one of the hydrogen atoms being replaceable by a metal.

All the common cations appear to form hypophosphites except  $\text{Sn}^{++}$ ,  $\text{Cu}^{++}$ , and  $\text{Hg}^+$ ; those of  $\text{Ag}^+$  and  $\text{Fe}^{+++}$  are very unstable.

The hypophosphites are very powerful reducing agents and, if in a mixture may, when in solution, cause profound changes in the chemical nature of the substances present. In most cases the final product of the oxidation of  $(\text{H}_2\text{PO}_2)^-$  is  $\text{PO}_4$ ----. In many cases the reducing action is energetic in both acid and alkaline solutions, but in a few cases in acid solution only.

Most salts of  $(\text{H}_2\text{PO}_2)^-$  when heated give off phosphine and hydrogen and are generally converted into meta- and pyro-phosphates.

(a) *Group Reactions.*

1. With  $\text{AgNO}_3$  there is first formed a heavy, white "amorphous" precipitate, soon becoming granular. In the outer zone, tiny dendritic crystals appear as single, rough, rod-like bodies and radiates of short, stout, acicular crystals. Skeleton forms in X's and H's are also abundant. In a very short time the white mass becomes discolored and turns brown with a purple cast, owing to the reduction of the  $\text{AgNO}_3$ , and at the same time the tiny crystals disintegrate in large part. Minute oily droplets are formed, and collect in large drops at the circumference of the test drop.

2.  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives no precipitate, no separation of crystals, and no distinct crystals appear when the test drop passes to dryness.

3.  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives results similar to those obtained with  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ . (See  $(\text{HPO}_3)^-$ .)

4.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  yields a white granular precipitate, changing in part into fusiform grains and very tiny, short, stout rods with rounded ends. A magnification of 150 to 200 $\times$  is required for their resolution.

5. With  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$  there is obtained a precipitate consisting of white (colorless), short, stout rods with rounded ends, many cubical grains, and cubes in such a position as to appear to be hexagons. The

rods are usually grouped in threes or sixes, and appear to be skeletons of octahedra.

**Phosphites — ( $\text{HPO}_3$ )—.**—Phosphorous acid,  $\text{H}_3\text{PO}_3$ , acts as a dibasic acid toward metallic cations. Both acid and “normal” salts are formed, but the third hydrogen atom cannot be replaced save by organic radicals.

Although there appears to be doubt that the acid called orthophosphorous acid should be written  $\text{H}_3\text{PO}_3$ , and its anion ( $\text{HPO}_3$ )—, the more familiar designation has been retained for greater convenience.

Phosphites of the alkali metals are water-soluble; most other phosphites are insoluble in water, but soluble in  $\text{H}_3\text{PO}_3$ , and are transposed by most acids.

The calcium, strontium, and barium salts of ( $\text{HPO}_3$ )— are difficultly soluble, thus affording a differentiation from the ready solubility of the hypophosphites of these elements.

The phosphites are strong reducing compounds and eventually change to phosphates in the presence of air.

(a) *Group Reactions.*

1. With  $\text{AgNO}_3$  a white “amorphous” or granular precipitate is at once produced, which rapidly becomes brown or black. The change appears to be even more rapid than in the case of ( $\text{H}_2\text{PO}_2$ )—.

The granular precipitate develops in part, along the outer zone, into thin skeleton crystals in the form of distorted X's in which the arms are more or less completely filled out, so that the crystal has the appearance of an envelope somewhat askew. Irregular dendritic forms float about.

At first sight the crystals appear to be similar to those obtained with ( $\text{H}_2\text{PO}_2$ )—, but a closer study will reveal that they are recognizably different. The short, stout rods of the silver salt of ( $\text{H}_2\text{PO}_2$ )— are absent, as are also the radiates. The oily droplets are also absent.

2. When  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  is added, there is formed first a mere turbidity, but in a few seconds a heavy white (colorless) precipitate is thrown down, consisting of minute crystalline grains; these soon grow into thin disks of variable outline. The majority are oval or somewhat lenticular; others are almost square with well-rounded corners, and still others rhomb-shaped with rounded angles. The little disks have a very characteristic appearance, and are not easily confused with the salts of other ions formed with  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  (Fig. 201, page 337).

3.  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  forms at once thin disks and exceedingly fine, colorless needles grouped in irregular bundles, sheaves, and moss-like clumps. Soon around these aggregates, thin plates and scales are formed, so

thin and with a refraction so nearly that of the mother liquor as to be almost invisible. As these platelets grow, the aggregates develop into many-petaled, flower-like clusters with imbricated obtuse or lanceolate petals. These crystal aggregates are very characteristic and appear to be specific for  $(\text{HPO}_3)^-$  (Fig. 200, page 337).

4.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  yields an immediate dense precipitate, consisting of tiny crystalline grains and small dendritic crystals of irregular shape. The reaction is of no specific value for the identification of  $(\text{HPO}_3)^-$ , since the crystals are too small and too irregular in form. Although they are unquestionably different in appearance from the lead salt of  $(\text{H}_2\text{PO}_2)^-$ , they are not sufficiently well developed to afford a safe differentiation.

5.  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$  gives no precipitate, and no crystals separate on standing. Distinction from  $(\text{H}_2\text{PO}_2)^-$ .

**Arsenates —  $\text{AsO}_4^{3-}$ .** — Orthoarsenic acid gives rise to salts containing the anion  $\text{AsO}_4^{3-}$ . With monovalent elements, mono-, di-, and tri-metal salts may be successively formed; but with the elements of higher valencies the nature of the salts depends upon variables, a discussion of which space will not permit.

Most orthoarsenates are isomorphous with the corresponding orthophosphates.

Although meta- and pyro-arsenic acids have been prepared, the evidence now available appears to indicate that salts of these two acids do not exist in aqueous solutions for any length of time, but become transformed into orthoarsenates.

The alkali orthoarsenates are soluble in water, most of them forming well-crystallizable salts; but the orthoarsenates of the majority of the other elements are either insoluble or soluble with difficulty. However, it must not be overlooked that many of these insoluble arsenates can unite with alkali arsenates to form water-soluble double salts.

*(a) Group Reactions.*

1. With  $\text{AgNO}_3$  an immediate, dark red granular precipitate is formed, which develops at once into irregular crystalline grains, most of which eventually change into three-armed skeletons and into three-, four-, and six-sided plates and tablets which are actually rhombic dodecahedra (Fig. 197, page 337). On standing, these plates and tablets thicken and become deep garnet in color. Later bristling hairs may appear in grouped, three-armed radiates, the arms of which form  $120^\circ$  angles with each other (Fig. 196, page 337). These radiates are very characteristic of silver arsenate. To obtain a suitable development of the granular precipitate it is necessary to tip the slide



so as to cause the reagent to flow freely but slowly into the test drop.

If a dark red "amorphous" or very finely granular precipitate persists, without developing into crystals of definite shape and color, it is wise to repeat the test using ammoniacal silver nitrate as reagent; under these conditions, well-developed crystals can almost invariably be formed, though they remain small.

$\text{Ag}_3\text{AsO}_4$  can be recrystallized from  $\text{NH}_4\text{OH}$  or  $\text{HNO}_3$ . (See Silver, page 282; Arsenic, page 228.)

2.  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives a slight, white "amorphous" precipitate in concentrated solutions, with no further change until the test drop is about to pass to dryness, when curious dendritic masses of fibrous crystals appear, some resembling lichens and liverworts, or flowers with thin lanceolate petals and compact fibrous centers.

3.  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives merely a faint "amorphous" precipitate which undergoes no change on standing; but in ammoniacal solutions large skeletal crystals are formed (Fig. 73, page 109).

4. With  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  a very heavy, white, gelatinous precipitate is obtained, with no change on standing other than a tendency to granulate; but the granulation is not marked.

5.  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$  reacts with  $\text{AsO}_4^{---}$  in a manner analogous to its behavior with  $\text{PO}_4^{---}$ . Very long needles are formed, extending completely across the field. They unite in wisps and radiates, but most of the needles occur singly. They are thicker and rougher than those obtained with  $\text{PO}_4^{---}$ , but the differences are too slight to afford a means of differentiating between the two salts. Between crossed nicols they are strongly birefringent and mottled with small patches of polarization colors. (See  $\text{CO}_3^{--}$ , page 324.)

(b) *Magnesia Mixture* (see  $\text{PO}_4^{---}$ , page 338) gives a precipitate of  $\text{NH}_4\text{MgAsO}_4 \cdot 6 \text{H}_2\text{O}$ , identical in appearance with  $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$  and isomorphous with it. Arsenites do not give this reaction. (Fig. 76, 77, page 109.)

(c) *Ammonium molybdate* produces a yellow precipitate of ammonium arsenomolybdate, which cannot be distinguished from the corresponding  $\text{PO}_4^{---}$  compound. (See  $\text{PO}_4^{---}$ , page 339.)

(d) The addition of KI to test drops strongly acidulated with HCl yields yellow-to-orange crystallites and hexagons. Distinction from phosphates. (See Arsenic, page 227.)

**Arsenites** —  $\text{AsO}_2^-$ ;  $(\text{HAsO}_3)^-$ ;  $(\text{AsO}_3)^-$  or  $(\text{As}_2\text{O}_6)^{--}$ . — The alkali "arsenites" of commerce have the formula  $\text{R}^+ \text{AsO}_2^-$  and are properly metarsenites. Alkali salts of the dibasic acid

$\text{H}_2(\text{HAsO}_3)$  are also possible. Both types of alkali "arsenites" are readily soluble in water.

All other elements apparently form "arsenites" derived from the acid  $\text{H}_6\text{As}_2\text{O}_6$  or  $\text{H}_3\text{AsO}_3$ , the number of hydrogen atoms replaced depending upon a number of variable conditions. These "arsenites," known as orthoarsenites, are insoluble in water or soluble with difficulty, except that the arsenites of the alkaline earths are appreciably water-soluble. Many of the insoluble arsenites, however, can unite with the arsenites of the alkalis to form water-soluble, double arsenites.

(a) *Group Reactions.*

1.  $\text{AgNO}_3$  gives first a white, then a heavy, yellow, gelatinous precipitate. Within the central open space in the advancing zone of precipitate, small, yellow granular disks and lenticular grains are formed. Many of these disks appear to be spherulites, but do not show a black cross between crossed nicols.

Many arsenites give, in addition to a yellow gelatinous precipitate, a few dark red crystalline grains, evidence of the presence of arsenates.

Because of the mixed nature of the yellowish-white precipitate it is best to test with ammoniacal silver nitrate; with this reagent arsenites give at once a clear, bright yellow, crystalline precipitate consisting of short rods with rounded ends, singly and in masses and radiates. The majority of crystals consist of elongated plates with parallel sides and notched ends. As the test drop evaporates, acicular crystals and dendritic groups are formed.

2. Barium arsenite is very soluble under the conditions governing its formation in the test drop, and no precipitate and no separation of crystals can be obtained.

3.  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ , like  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ , gives no precipitate and no separation of crystals.

4.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives a heavy, white, gelatinous precipitate only.

5.  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$  yields tiny granular disks. These disks occur singly and are seldom united.

### DETECTION OF THE ANIONS OF THE SULPHUR GROUP

$\text{S}^-$ ;  $\text{S}_2\text{O}_3^-$ ;  $\text{S}_2\text{O}_4^-$ ;  $\text{SO}_3^-$ ;  $\text{SO}_4^-$ ;  $\text{S}_2\text{O}_6^-$ ;  $\text{S}_3\text{O}_6^-$ ;  $\text{S}_4\text{O}_6^-$ ;  $\text{S}_5\text{O}_6^-$ ;  $\text{S}_6\text{O}_6^-$ ;  $\text{S}_2\text{O}_5^-$ ;  $\text{S}_2\text{O}_7^-$ ;  $\text{S}_2\text{O}_8^-$ ;  $\text{SeO}_3^-$ ;  $\text{SeO}_4^-$ ;  $\text{TeO}_3^-$ ;  $\text{TeO}_4^-$

Of these ions  $\text{SO}_4^-$  is of greatest importance because of the vast number of simple and double salts that are known and are common articles of commerce. Sulphites and sulphides range next in importance and in numbers; of the salts of the remaining ions  $\text{Na}_2\text{S}_2\text{O}_3$  and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  are probably the only ones likely to be met with frequently in ordinary commercial products.

Salts of hyposulphurous acid are unstable in solution, forming thio-sulphates, sulphites, and free sulphur.

Salts of  $\text{SO}_4^{--}$  are seldom contaminated with salts of the other ions of the group; but the salts of the remaining ions ordinarily contain more or less impurities, such as sulphates or salts of the other more closely related ions, the nature of which depends upon the method used for the formation of the ion in question. These foreign ions, which are almost invariably present, introduce a complication in the analysis of very small amounts of material, and may trouble the analyst.

Most salts of the thionic acids ( $\text{S}_2\text{O}_6^{--}$ ,  $\text{S}_3\text{O}_6^{--}$ ,  $\text{S}_4\text{O}_6^{--}$ ,  $\text{S}_5\text{O}_6^{--}$ ,  $\text{S}_6\text{O}_6^{--}$ ,  $\text{S}_n\text{O}_6^{--}$ ) are unstable and rapidly decompose in aqueous solutions. Their detection and identification are therefore difficult and in many cases impossible.

### Sulphates — $\text{SO}_4^{--}$ .

#### (a) Group Reactions.

1. The precipitate with  $\text{BaCl}_2$  or  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  is exceedingly fine (in "neutral" solutions) or, at the most, finely granular, insoluble in water, and not appreciably soluble in dilute  $\text{HNO}_3$ .

2. Silver nitrate produces no precipitate in *dilute* test drops, but, from concentrated solution, colorless, highly refractive, rhomb-shaped tablets or short stout prisms with angular ends (pseudo-octahedra) separate. The crystals of  $\text{Ag}_2\text{SO}_4$  have a characteristic habit and are easily recognized. If either  $\text{CrO}_4^{--}$  or  $\text{Cr}_2\text{O}_7^{--}$  is present in small amount, the  $\text{Ag}_2\text{SO}_4$  crystals are colored yellow to red and are pleochroic (isomorphous mixture). (Fig. 203, page 341. In the photograph, the black "prisms" are tablets seen edgewise.)

3. With  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  by Method I,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is obtained in characteristic needles, sheaves, radiates, arrow-head twins, or masses of broad foliated plates. (See Calcium, page 106.) The crystals are soluble in water and are therefore obtainable only when the test drop contains a fairly high concentration of  $\text{SO}_4^{--}$ . Ions giving insoluble compounds with calcium either mask this reaction or interfere with it to the extent of preventing the separation of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; in such cases the addition of a *very little*  $\text{HNO}_3$  to the test drop after the  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ , and gentle warming, may give rise to conditions more favorable for the separation of the gypsum crystals; the latter are, however, quite soluble in  $\text{HNO}_3$ , so that too much acid will result in failure to detect  $\text{SO}_4^{--}$  even when present in relatively large amount (Figs. 70, 71, page 105).

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is soluble in alkali thiosulphates; hence in mixtures containing  $\text{SO}_4^{--}$  and  $\text{S}_2\text{O}_3^{--}$  no crystals of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  may appear

until the test drop passes almost to dryness, and the separation of various other salts may completely mask the reaction.

4. With  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  there is instantly formed a heavy, dense, white, finely granular precipitate, practically insoluble in water and very difficultly soluble in  $\text{HNO}_3$ .

On standing for a short time the granular precipitate changes into tiny, bristling dendritic grains and irregular masses of short, stout, sharply angular crystals.

5. With  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$  by Methods I,  $\text{Tl}_2\text{SO}_4$  is obtained in colorless, long, thin, highly refractive rhombs and orthorhombic prisms with oblique or angular ends (Fig. 205, page 341). These plate-like prisms soon build up to thick, well-formed rectangular tablets and prisms with pyramidal or obliquely truncated ends; irregular tablets are also formed (Fig. 204, page 341).

When using  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$  as a reagent it is especially important to perform several tests, using test drops of varying concentrations.

(b) The addition of dilute  $\text{H}_2\text{SO}_4$  sets free no  $\text{SO}_2$ .

(c) The addition of dilute  $\text{H}_2\text{SO}_4$  and metallic zinc produces no more  $\text{H}_2\text{S}$  than a "blank" test made at the same time with zinc and  $\text{H}_2\text{SO}_4$  alone.

(d) Insoluble sulphates can be fused with a very little metallic potassium and the nitroprusside test made upon the alkaline aqueous solution.<sup>11</sup>

**Sulphites —  $\text{SO}_3^-$ .** — The normal and acid sulphites of the alkalis are readily soluble in water, but the normal sulphites of all other metals are insoluble or nearly so.

The sulphites of the alkaline earths and a few metallic sulphites dissolve in water containing  $\text{SO}_2$ , forming soluble acid sulphites (bisulphites). When solutions of these "bisulphites" are boiled, the normal sulphite is reprecipitated. Boiling does not cause a decomposition of alkali sulphites.

$\text{SO}_3^-$  in an insoluble sulphite can be converted into water-soluble  $\text{Na}_2\text{SO}_3$  by boiling with a concentrated solution of  $\text{Na}_2\text{CO}_3$ ; or  $\text{SO}_2$  can be liberated by an acid and identified.

$\text{SO}_3^-$  is readily oxidized to  $\text{SO}_4^-$  by concentrated  $\text{HNO}_3$ , strong bromine water, or  $\text{Na}_2\text{O}_2$ . After the excess of the oxidizing agent has been removed by boiling,  $\text{SO}_4^-$  can be tested for by  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ . (See page 349.) Conversion to  $\text{SO}_4^-$  by this reaction is not confined to  $\text{SO}_3^-$ , but is common to many other sulphur acids.

Sulphites in solution reduce  $\text{HIO}_3$ , iodine being set free, which will color starch granules blue.  $\text{SO}_2$ , liberated by an acid and expelled by

<sup>11</sup> Feigl: *Mikrochemie* 20, 198 (1936).

Method IX, page 42, will also give the blue color with  $\text{HIO}_3$  and starch, or  $\text{KI}$  and starch. This reaction is not specific for  $\text{SO}_3^{--}$ .

(a) *Group Reactions.*

1.  $\text{AgNO}_3$  added by Method I gives an immediate, snow-white "amorphous" or granular precipitate of  $\text{Ag}_2\text{SO}_3$ , changing rapidly to brown on boiling, metallic silver and  $\text{H}_2\text{SO}_4$  being formed. The white  $\text{Ag}_2\text{SO}_3$  is readily soluble in  $\text{HNO}_3$  and is also soluble in excess of alkali sulphites.

Since most sulphites contain sulphates,  $\text{Ag}_2\text{SO}_4$  separates in characteristic crystals on standing. (See  $\text{SO}_4^{--}$ , page 349, Fig. 203, page 341.) The appearance of  $\text{Ag}_2\text{SO}_4$  crystals in very small amount cannot be taken as proof of the presence of sulphates in the sulphite under examination, for when  $\text{AgNO}_3$  is used as reagent there appears to be always an oxidation of some  $\text{SO}_3^{--}$  to  $\text{SO}_4^{--}$ .

2. With  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  or  $\text{BaCl}_2$  a heavy, white, granular precipitate is first formed. On standing, tiny dendritic crystals appear in a zone just at the edge of the mass of precipitate. Eventually these crystals grow slightly larger, and rhomboidal skeleton plates can be readily resolved under a magnification of 150 to 200 $\times$ .  $\text{BaSO}_3$  can be distinguished from  $\text{BaSO}_4$  by adding  $\text{HCl}$ , in which  $\text{BaSO}_3$  is readily soluble but  $\text{BaSO}_4$  is practically insoluble.

The tiny crystals of  $\text{BaSO}_3$  are anisotropic but are only weakly birefringent.

3. The addition of  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  by Method I gives rise to the formation of strongly birefringent, tiny disks and spherulites; the latter develop into botryoidal grains or aggregates (Fig. 207, page 341). The separation is slow and the grains always remain small. This reaction offers a simple means of distinguishing between  $\text{SO}_3^{--}$  and  $\text{S}_2\text{O}_3^{--}$ , for the calcium salt of  $\text{S}_2\text{O}_3$  is too soluble to separate under the conditions which obtain. After allowing sufficient time for the separation of the sulphite crystals, the supernatant solution can be decanted and tested for  $\text{S}_2\text{O}_3$  by means of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ . (See page 353.)

4. Added to concentrated solutions  $\text{Ti}(\text{C}_2\text{H}_3\text{O}_2)_2$  yields angular grains. At the circumference of the test drop dendrites may appear. The majority of the crystals which separate are irregular angular grains or square, rectangular, or six-sided plates. The crystal form varies greatly with concentrations.

5. With solutions of sodium nitroprusside the alkali sulphites yield a red color which, on standing, disappears, and a yellow compound is precipitated having the formula  $\text{Na}_5[\text{Fe}(\text{CN})_5\text{SO}_3]$ .<sup>12</sup>

<sup>12</sup> Scagliarini: *Atti accad. Lincei* 22, 155 (1935).

6. Benzyl-pseudo-thiourea hydrochloride (see polythionates, pages 360–365), added to concentrated test drops, precipitates slender needles and produces an intensely disagreeable mercaptan-like odor which appears to be characteristic of sulphites in the absence of fluorides and carbonates, which also yield a stench with this reagent.

(b) *Reduction to  $H_2S$ .*

$SO_3^{--}$  is readily reduced to  $H_2S$  by metallic zinc and HCl. Test in the crucible, using as reagent a hanging drop of  $Pb(C_2H_3O_2)_2$  made alkaline with NaOH; the white precipitate turns black. Or absorb the  $H_2S$  in a hanging drop of NaOH and test with sodium nitroprusside; or expose a moistened crystal of  $AgNO_3$ , or one of  $Pb(C_2H_3O_2)_2$ , to the gas evolved.

**Thiosulphates —  $S_2O_3^{--}$ .** — Salts of this ion, properly termed thiosulphates, must not be confused with salts of the ion  $SO_3^{--}$ , hyposulphites (hydrosulphites), although the sodium salt  $Na_2S_2O_3$  is still known to photographers as “hypo” — a designation retained from the days when the acid  $H_2S_2O_3$  was commonly known as hyposulphurous acid.

Most thiosulphates are unstable, some of them decomposing almost as soon as formed. The usual types of decomposition are to sulphates and polysulphides, or to sulphur and  $H_2S$ . In the latter case there will generally result a sulphate, free sulphur, and the sulphide of the metal, but intermediate compounds are almost always formed also.

It is important that the analyst bear this instability in mind, for it is obvious that in but few cases will he have to deal with a thiosulphate entirely free from other sulphur acids.

Soluble and water-insoluble thiosulphates are decomposed by acids and dissolved, and sulphur is usually precipitated.

Thiosulphates unite to form many complex ions with the heavy metals;<sup>13</sup> some of these complexes may complicate or interfere with microscopical qualitative analyses.

(a) *Group Reactions.*

1. With  $AgNO_3$  there is first formed a white, dense, granular precipitate. This rapidly turns yellow, then dark yellow, and finally brown or black, owing to the formation of silver sulphide. Sulphur is usually set free.

$SO_4^{--}$  ions are generally present in considerable amounts in commercial grades of thiosulphates; hence crystals of  $Ag_2SO_4$  soon appear in the test drop. These crystals, though still preserving their characteristic habit, are discolored by  $Ag_2S$  and appear yellow, brown, or black.

<sup>13</sup> Britzinger and Eckart: *Zeit. anorg. allgem. Chem.* 227, 107 (1936).

Careful observation will disclose that these crystals are "stained" on the outside and are not the result of the separation of crystals of salts containing a cation giving rise to a colored compound. It is important that the preparation be allowed to stand for a short time until the yellow hue changes to brown or black; otherwise the analyst may form the hasty conclusion that  $\text{CrO}_4^{--}$  ions are also present, since certain yellow hues resemble somewhat those imparted by a very little  $\text{CrO}_4^{--}$ .  $\text{PO}_4^{--}$ ;  $\text{CNS}^-$ ;  $\text{CN}^-$ ;  $\text{Fe}(\text{CN})_6^{--}$ ;  $\text{Fe}(\text{CN})_6^{--}$ , interfere.

$\text{Ag}_2\text{S}_2\text{O}_3$  is readily soluble in excess of alkali sulphate, because of the formation of the double salt  $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Ag}_2\text{S}_2\text{O}_3$ . Hence it is important that the  $\text{AgNO}_3$  reagent drop shall be concentrated, and that sufficient solution shall have been led into the test drop to insure a permanent precipitate.

2.  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  forms  $\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , a white, finely granular precipitate, only slightly soluble in water, but readily soluble in acids.

3.  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  causes no precipitate in solutions of thiosulphates — a distinction from sulphites. In a mixture of  $\text{SO}_3^{--}$  and  $\text{S}_2\text{O}_3^{--}$ , the  $\text{SO}_3^{--}$  can be precipitated with  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  and the clear solution tested for  $\text{S}_2\text{O}_3$  after decantation, filtration, or separation by means of the centrifuge.

4. A concentrated solution of a salt of  $\text{S}_2\text{O}_3$  treated with acetic acid gives a white precipitate of sulphur, and  $\text{SO}_2$  is formed. The latter can be tested by KI and starch, either in the solution, or, better, by expulsion by Method IX, page 42.

5. With metallic zinc and HCl, thiosulphates are reduced to  $\text{H}_2\text{S}$ . (See  $\text{SO}_3$ , page 352.)

6. A reaction which appears to be constant and peculiar to  $\text{S}_2\text{O}_3^{--}$  is that obtained when  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  is added to alkali thiosulphates by Method I. There is first obtained a dense, white granular, almost "amorphous," precipitate. After standing a few minutes thin, colorless, well-formed, highly refractive, lozenge-shaped plates in foliated aggregates separate within the granular mass of precipitate or in a zone just beyond it (Fig. 208, page 355). Arrow-head twins are frequent. These rhomboidal plates and tablets are strongly birefringent and exhibit brilliant polarization colors. This salt is soluble in excess of  $\text{Na}_2\text{S}_2\text{O}_3$ ; hence an excess of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  must be present to insure its separation. This is accomplished by having a high concentration in the reagent drop, and taking steps to prevent the reagent drop from "breaking away" from the test drop — a tendency strongly marked when a concentrated solution of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  is used as the reagent.

In addition to the rhomb-shaped tablets and plates there are always formed disks and spherulites of exceedingly fine needles; these spheru-

lites unite into dumb-bell-shaped aggregates, which in turn develop into relatively large sheaves (Fig. 209). Save when in disk form, these aggregates are remarkable for their light-scattering power, and by transmitted light appear to be perfectly opaque and therefore jet black. The disks are strongly birefringent and exhibit brilliant polarization colors.

$\text{SO}_4^{--}$  ions interfere, probably because of the removal of  $\text{Pb}^{++}$ ; but if the reagent is properly applied and the  $\text{SO}_4^{--}$  ions are not greatly in excess of the  $\text{S}_2\text{O}_3^{--}$ , both types of crystals typical of  $\text{S}_2\text{O}_3^{--}$  are obtained. If the  $\text{S}_2\text{O}_3^{--}$  ions are present in very small amount, the rhombs are not always formed, because it appears to be difficult to hit upon just the proper equilibrium conditions to bring about their formation.

In testing for  $\text{S}_2\text{O}_3^{--}$  with  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  it is more important than in most cases to experiment with test drops of several different concentrations, and to allow the preparations to stand for several minutes and never to neglect to search the preparation using crossed nicols. In mixtures a dense granular precipitate may mask the rhombs, but between crossed nicols they are readily found because of their strong birefringence.

By means of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  it is possible to detect soluble  $\text{S}_2\text{O}_3^{--}$  in the presence of soluble sulphites, persulphates, and thionates.

The authors have found that the addition of a *very little*  $\text{NH}_4\text{-(C}_2\text{H}_3\text{O}_2\text{)}$  to a test drop containing a dense mass of precipitate sometimes improves the test, but if too much is added the test fails completely.

7. The addition of  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$  gives rise to tiny white stars, crosses, X's, irregular crystalline grains, and peculiar feathery dendrites. These tiny skeleton and dendritic crystals are highly refractive and scatter light very strongly. Their birefringence is weak.

Polythionates also give skeleton and dendritic crystals with  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ , but these crystals grow much larger and have a very different appearance; moreover, long prisms with pyramidal ends are eventually formed. These prisms extinguish parallel with the direction of their elongation.

8. With nickel ethylenediamine nitrate, needles, rods, long rectangular prisms, and plates are formed (Fig. 225, page 361). Dithionates give a similar precipitate but no other anions of the Sulphur Group. (See Polythionates, pages 360–365.)

**Persulphates** —  $\text{S}_2\text{O}_8^{--}$  ( $\text{SO}_4^{--}$ ). — All salts of the ion  $\text{S}_2\text{O}_8^{--}$  which are likely to be met with are soluble in cold water; the least soluble of them is  $\text{K}_2\text{S}_2\text{O}_8$ .



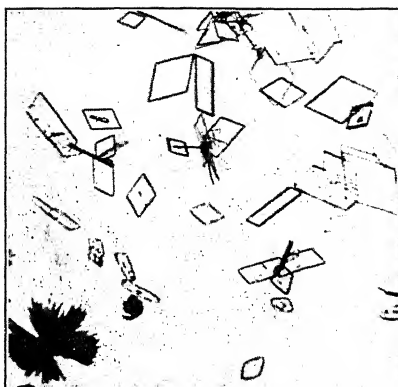


FIG. 208.  $S_2O_3^{2-}$  with Lead Acetate. 150X.



FIG. 209.  $S_2O_3^{2-}$  with Lead Acetate. 150X.

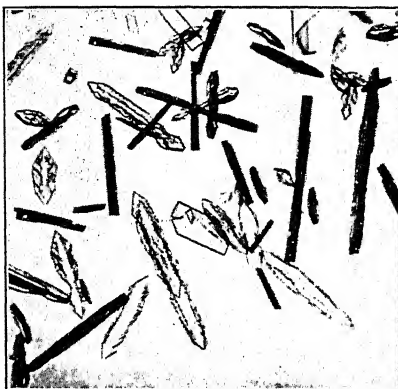


FIG. 210.  $CrO_4^{2-}$  with Silver Nitrate. 100X.

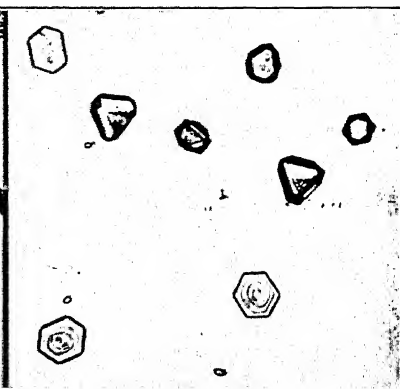


FIG. 211.  $Cl^-$  with Silver Nitrate and the  $AgCl$  recrystallized from  $NH_4OH$ . 500X.

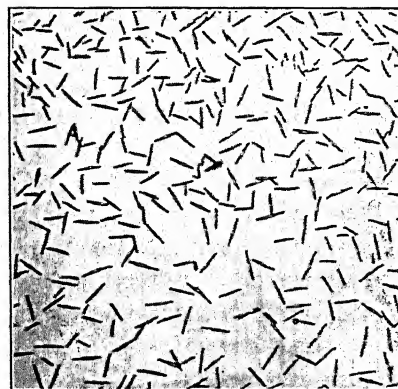


FIG. 212.  $Br_2$  ( $Br^-$ ;  $BrO_3^-$ ) with Metaphenylenediamine Hydrochloride. 200X.

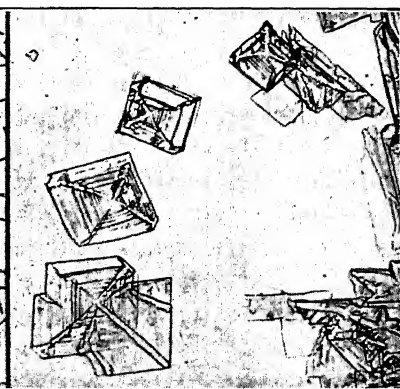


FIG. 213.  $(C_2H_3O_2)^-$  with Mercurous Nitrate. 100X.

The persulphates are very strong oxidizing agents, converting manganese, cobalt, nickel, and lead salts into peroxides.

In the solid state the salts of  $S_2O_8^{--}$  are quite stable. Most of them crystallize well.

In solution, and in the presence of moisture, persulphates slowly decompose. Old samples of persulphates almost invariably contain a relatively large amount of sulphate ions.

In aqueous solution persulphates slowly decompose; usually oxygen is given off, a sulphate of the cation present is formed, and  $H_2SO_4$  is set free. An exception to this reaction is to be found in the decomposition of aqueous solutions of  $(NH_4)_2S_2O_8$ . It is mentioned here because it affords a striking illustration of the extraordinary oxidizing power of  $S_2O_8^{--}$ ; in this case no oxygen is evolved but part of the  $NH_4$  is oxidized to  $HNO_3$ ; the final products of decomposition are  $(NH_4)HSO_4$ , free  $H_2SO_4$ , and free  $HNO_3$ .

No microscopical reactions constant and peculiar to  $S_2O_8^{--}$  have yet been found, and the identification of this ion must be largely through a process of elimination.

The reaction *a-1* distinguishes  $S_2O_8^{--}$  from  $SO_4^{--}$  but, to obtain the formation of black (or brown) silver oxide, the test drop must be concentrated with respect to salts of  $S_2O_8^{--}$ .

Reaction (*b*) will differentiate  $S_2O_8^{--}$  and  $SO_4^{--}$  from all the other usual acids of sulphur.

(*a*) *Group Reactions.*

1.  $AgNO_3$  produces almost at once a heavy, white, crystalline precipitate. The crystals first formed closely resemble those of  $Ag_2SO_4$  (which are always present) but are more elongated and slightly lenticular, that is, they have bulging sides midway their length; later rhombs and six-sided tablets abound, as also do short, stout prisms with angular ends; but, since the resemblance to those of  $Ag_2SO_4$  is so close, it is impossible to decide whether the crystals obtained are those of a silver salt of  $S_2O_8^{--}$  or of  $SO_4^{--}$ , the latter slightly modified by the presence of  $S_2O_8^{--}$  ions.

In a short time a blackish cloud of hydrous  $Ag_2O$  appears and the crystals become stained black; black flocs float about in the liquid and tiny black disks deposit upon the object slide. Often, just as the test drop passes to dryness, a ring of brown appears at the circumference of the test drop. The phenomenon of blackening is very different from that obtained with  $S_2O_3^{--}$  and the two cannot be confused; moreover, with  $S_2O_8^{--}$  the silver salt does not at first turn yellow.

2.  $Ba(C_2H_3O_2)_2$  (or  $BaCl_2$ ) forms a white, fine, granular precipitate, which rapidly develops into colorless, irregularly angular grains having

a more or less diamond-shaped outline. Short rods with rounded ends and rods with a central swelling are also abundant. These crystals are accompanied by finely granular  $\text{BaSO}_4$ . When much decomposition of  $\text{S}_2\text{O}_8^{--}$  has taken place, or if the persulphate contains much sulphate, the fine precipitate of  $\text{BaSO}_4$  may mask the crystals of  $\text{BaS}_2\text{O}_8 \cdot 4 \text{H}_2\text{O}$ .

Since  $\text{BaS}_2\text{O}_8 \cdot 4 \text{H}_2\text{O}$  is moderately soluble, crystals of this salt will not separate unless the test drop is concentrated. In dilute solutions no immediate separation can occur, and only  $\text{BaSO}_4$  is precipitated. The same difficulty is here encountered as in  $\alpha$ -1 with the silver salts, for  $\text{BaSO}_4$  may be precipitated in crystalline form; it is obvious that  $\text{Ba}^{++}$  does not differentiate between  $\text{S}_2\text{O}_8^{--}$  and  $\text{SO}_4^{--}$ .

3. With  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  there is obtained a precipitate of white granular  $\text{PbSO}_4$ , and beyond this crystalline grains and tiny rods are formed; the latter usually occur singly. On standing, the crystalline grains increase slightly in size and assume an elliptical outline, or become distinct rhombs with their acute angles somewhat rounded. Here again the differentiation between  $\text{S}_2\text{O}_8^{--}$  and  $\text{SO}_4^{--}$  is questionable.

4. With  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  no precipitate is formed, and there is no separation of crystals even in concentrated solutions; but, on standing, crystals of  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  appear in abundance. If the material being tested consists of a persulphate containing a large amount of pre-formed sulphate, gypsum crystals appear at once from concentrated solution; but this difference in the rate of separation of gypsum crystals is not a safe basis upon which to found an opinion relative to the purity of a given persulphate; nor is it possible to decide by calcium acetate alone whether the material in hand is a persulphate or a mixture of sulphates and persulphates.

5. With  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$  no crystals other than  $\text{Tl}_2\text{SO}_4$  appear to be formed. This accords with the results obtained by Foster and Smith,<sup>14</sup> who found thallium persulphate so unstable as to decompose at once in air.

(b)  $\text{KMnO}_4$  added by Method I to *freshly prepared* solutions of persulphates is *not* decolorized or changed in hue, whereas decolorization, with or without the precipitation of oxides of manganese, takes place at once in presence of  $\text{SO}_3^{--}$ ,  $\text{S}_2\text{O}_3^{--}$ ,  $\text{S}^{--}$ , and the thionate ions  $\text{S}_2\text{O}_6^{--}$ ,  $\text{S}_3\text{O}_6^{--}$ ,  $\text{S}_4\text{O}_6^{--}$ ,  $\text{S}_5\text{O}_6^{--}$ .

Of the sulphur acids likely to be met with, the sulphates and persulphates alone do not decolorize  $\text{KMnO}_4$ .

**Sulphides** —  $\text{S}^{--}(\text{H}_2\text{S})$ . — The sulphides of the alkalis and those of the alkaline earths are readily soluble in water, but in their aqueous

<sup>14</sup> *Jour. Amer. Chem. Soc.* 21, 934 (1899).

solutions they are unstable and rapidly decompose; sulphur is set free, and complex thio-compounds are formed. Usually some  $S^{--}$  is oxidized to  $SO_4^{--}$ .

The sulphides of the heavy metals are insoluble in water. Most of them are stable in dry air, but in the presence of moisture or acids many of them are decomposed.

$S^{--}$  in insoluble sulphides is most satisfactorily detected by fusion:

(a) With  $Na_2CO_3$  and  $KNO_3$  or  $KClO_3$ , whereby the  $S^{--}$  is converted into  $SO_4^{--}$ . After the addition of  $HC_2H_3O_2$  to decompose the excess of  $Na_2CO_3$  the solution is tested for  $SO_4^{--}$ .

(b) With  $KOH$ , and testing with sodium nitroprusside<sup>15</sup>; or adding an acid, setting free  $H_2S$  and testing for this gas by the hanging-drop method using  $Pb(C_2H_3O_2)_2$  and  $AgNO_3$  solutions, or passing the gas over crystals of  $Pb(C_2H_3O_2)_2$  and  $AgNO_3$  in a capillary tube. (See page 222.)

$S^{--}$  in water-soluble sulphides gives a black precipitate with  $AgNO_3$  in the Bunsen-Treadwell grouping, but no appreciable reaction with  $BaCl_2$ , other than in a few cases a faint cloudiness due to sulphur set free; slight decompositions of this character are seldom discernible in a test drop under the microscope.

Slow decompositions of  $H_2S$  solutions, and solutions of sulphides, or of thio-compounds, or reducing decompositions of  $SO_4^{--}$  and of other sulphur-containing ions not infrequently give rise to a precipitate of crystalline sulphur. These crystals, if formed at ordinary temperatures, are faintly yellow, glistening, very highly refractive, very strongly birefringent, orthorhombic, bipyramidal grains with a melting point of  $108^\circ C$ . At  $98^\circ C$ . inversion to monoclinic sulphur takes place; above  $98^\circ$  monoclinic sulphur is stable and may persist in metastable form at lower temperatures. Tiny crystals of sulphur can be recognized by their color, high refraction and double refraction, melting point, flammability, burning with a blue flame, and giving fumes of  $SO_2$ . The crystals are brittle (hardness 2), and insoluble in water and weak acids; they are soluble in  $CS_2$ ; fused with  $Na_2CO_3$  and  $KNO_3$  sulphates are obtained, and fused with  $KOH$  sulphides are formed.

Free sulphur and most sulphides can be converted into  $H_2SO_4$  by repeated treatments with hot concentrated  $HNO_3$ . The treatment must be continued until a clear solution is obtained. In the case of free sulphur the crystalline form is much more resistant to oxidation than when "amorphous" or sublimed.

Oxidation can also be accomplished with bromine. With small

<sup>15</sup> For a discussion of the reagent and of its reaction products, see Sas: *Ann. soc. espan. fisquim.* 34, 419 (1936).

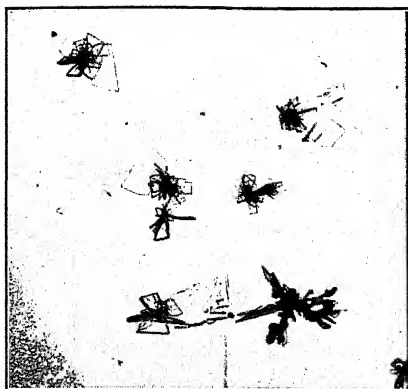


FIG. 214.  $S_2O_6^{--}$  with Nitron Sulphate. 50X.

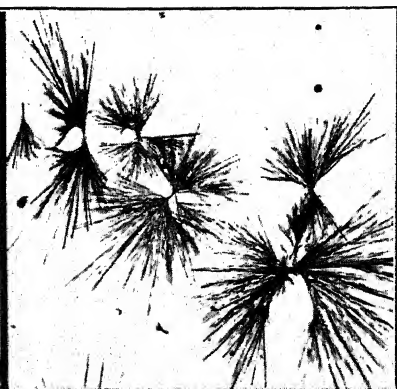


FIG. 215.  $S_2O_6^{--}$  with Nitron Sulphate. 50X.



FIG. 216.  $S_2O_6^{--}$  with Luteocobalt Chloride. 50X.



FIG. 217.  $S_2O_6^{--}$  with Luteocobalt Chloride. 50X.



FIG. 218.  $S_2O_6^{--}$  with Luteocobalt Chloride. 50X.



FIG. 219.  $S_2O_6^{--}$  with Luteocobalt Chloride. 50X.

amounts of material the oxidation is conveniently carried out in the distillation crucible. A few drops of very strong bromine water (or of bromine) are placed in the crucible and the moistened material is exposed in a hanging drop to the action of the vapors. Gentle heating favors the reaction. Oxidations with  $\text{HNO}_3$  and  $\text{Br}_2$  should be performed in a hood.

**THE POLYTHIONATES** —  $\text{S}_2\text{O}_6^{--}$ ;  $\text{S}_3\text{O}_6^{--}$ ;  $\text{S}_4\text{O}_6^{--}$ ;  $\text{S}_5\text{O}_6^{--}$ ;  $\text{S}_n\text{O}_6^{--}$ .

The first member of this series of anions is properly not a polythionate because its chemical behavior and the manner of formation of dithionic acid are not in accord with the remaining members of the series.<sup>16</sup> However, for analytical purposes it is more logical to include dithionates in the series than to place them in a class by themselves.

With the exception of most of the salts of dithionic acid, the polythionates are unstable and undergo spontaneous decompositions which are particularly rapid in moist air and in solutions. An aqueous solution of tri-, tetra-, or penta-thionate salts will, in a very short time, contain salts of all three thionates. In solutions the extent and character of the breakdown depend upon the pH of the solutions.<sup>17</sup>

The Group Reagents calcium, barium, lead, and thallium acetates give no crystalline precipitates with polythionates when the tests are made upon object slides by Method I, page 31.

**Dithionates** —  $\text{S}_2\text{O}_6^{--}$ . — Most dithionates are water soluble.

*Group Reactions* — See pages 316–321.

(a) With nitron sulphate added to dilute test drops very small fusiform crystals are obtained, singly in crosses and in radiates. In concentrated test drops there is no separation of crystals even on long standing.

(b) Nickel ethylenediamine nitrate<sup>18</sup> in neutral or very faintly acid solutions yields fine needles, rods, and long rectangular prisms or elongated rectangular plates having refractive indices,  $\omega = 1.53$ ,  $\epsilon = 1.54$ . Thiosulphates form with the reagent crystals of identical appearance but more highly refractive, with  $\omega = 1.605$ ,  $\epsilon = 1.625$ . A convenient procedure for differentiating between the two complexes is to immerse in bromoform ( $n = 1.59$ ); and if the crystals give indices below 1.59 they are probably dithionate, if above that of the bromo-

<sup>16</sup> Debus: *Ann.* **244**, 76 (1888); Rashig: *Schwefel und Stickstoff-Studien*, Leipzig, 1924; Riesenfeld u. Feld: *Zeit. anorg. Chem.* **119**, 225 (1921).

<sup>17</sup> Kurténacker, Mutschin, and Stastny: *Zeit. anorg. allgem. Chem.* **224**, 399 (1935); Janickis: *ibid.* **225**, 177 (1936).

<sup>18</sup> Spacu and Spacu: *Zeit. anal. Chem.* **89**, 192 (1932).

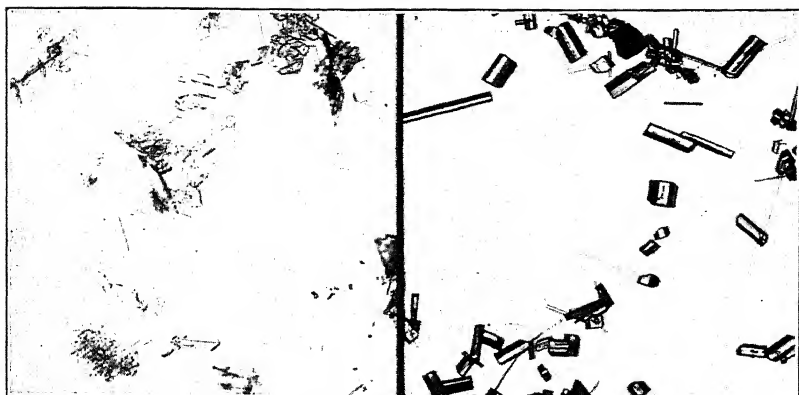


FIG. 220.  $S_2O_6^{--}$  with Benzylpseudo-thiourea. 50X.

FIG. 221.  $S_2O_6^{--}$  with Benzylpseudo-thiourea. 50X.

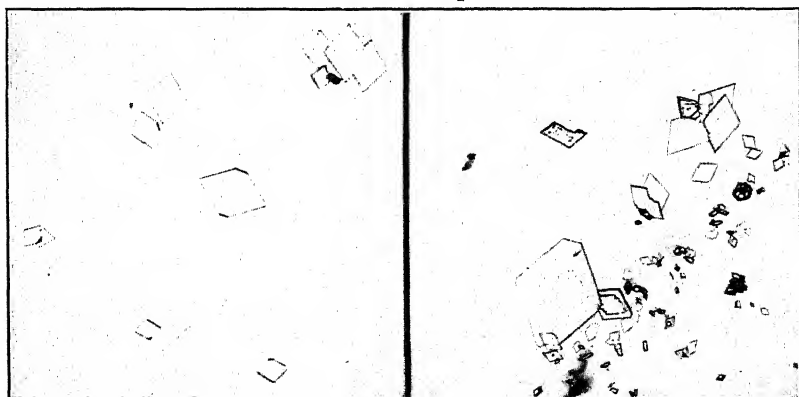


FIG. 222.  $S_4O_6^{--}$  with Benzylpseudo-thiourea. 50X.

FIG. 223.  $S_5O_6^{--}$  with Benzylpseudo-thiourea. 50X.

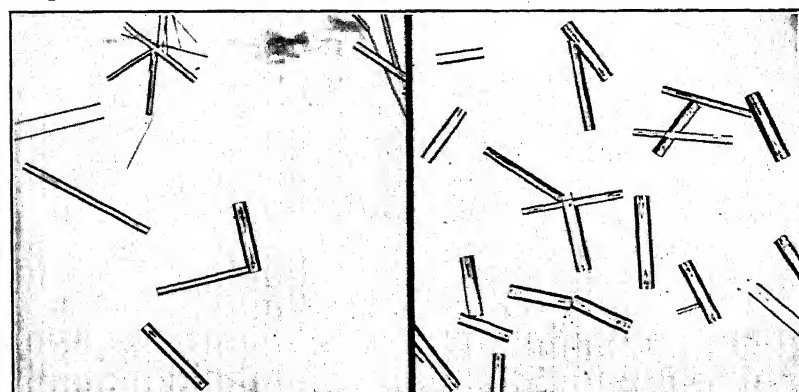


FIG. 224.  $S_2O_6^{--}$  with Nickel Ethylenediamine Nitrate. 50X.

FIG. 225.  $S_2O_6^{--}$  with Nickel Ethylenediamine Nitrate. 50X.

form they are due to thiosulphate. (Figs. 224, 225, page 361.) The crystals are uniaxial, negative.

(c) Benzyl-pseudo-thiourea precipitates thin rhombs and elongated rhombiform plates or micaceous scales (Fig. 220, page 361).

(d) Luteocobalt chloride causes no immediate separation of crystals but, on standing, large, light brown plates and tablets or prisms appear. (Fig. 216, page 359.)

**Trithionates —  $S_3O_6$ .** — Most of the salts with common cations are soluble in water, but  $Ag^+$ ,  $Hg^+$ ,  $Hg^{++}$  are insoluble.

(a) Nitron sulphate yields in all concentrations an immediate precipitate of oily drops with crystallization setting in at once, forming very characteristic thin plates without curving sides in irregular foliated clumps. Elongated plates and prisms exhibiting an extinction angle of  $8^\circ$  are also to be found (Fig. 214, page 359).

(b) Benzyl-pseudo-thiourea yields slender needles and prisms or highly refractive rods. The test drops to which the reagent has been added tend to supersaturate; rubbing the glass with rod or wire causes the separation of short, stout prisms and thick tablets (Fig. 221, page 361).

(c) Nickel ethylenediamine nitrate — No visible reaction.

(d) Luteocobalt chloride forms rectangular plates and prisms (Fig. 217, page 359). But no crystals separate in dilute solutions.

(e) With  $HgNO_3$  a black precipitate of sulphide is at first formed which on standing slowly becomes white. Dithionates give no visible reaction. Tetra- and penta-thionates give at first a yellow precipitate which, in the case of tetrathionates, darkens, whereas that from penta-thionates turns white. Thiosulphates must be absent.

**Tetrathionates —  $S_4O_6$ .** — The sodium and the potassium tetrathionates, when precipitated from concentrated solutions by alcohol, have very characteristic habits and cannot be confused with sodium and potassium salts of the other polythionic acids.

(a) With nitron sulphate oily drops are obtained which do not yield crystals until the preparation passes almost to dryness. Clumps of acicular crystals then appear which cannot be distinguished from those of the reagent.

(b) Benzyl-pseudo-thiourea yields well-formed, thin rhombs, many of which have one or both obtuse angles truncated, forming five- or six-sided plates (Fig. 222, page 361). If the test drop is too concentrated, malformed plates and dendritic clumps are obtained.

(c) Nickel ethylenediamine nitrate — No visible reaction.

(d) Luteocobalt chloride — No visible reaction.



**Pentathionates** —  $S_5O_6$  — are ordinarily formed in the decomposition of di-, tri-, and tetra-thionates. Basset and Durant<sup>19</sup> have shown that it is possible to distinguish between pentathionates and colloidal sulphur by means of a dilute solution of didymium chloride, which causes an agglutination of colloidal sulphur but has no visible effect upon pentathionates.

(a)  $AgNO_3$  produces a brown or black amorphous precipitate. Di-, tri-, and tetra-thionates do not give this reaction.

(b) When solutions of pentathionates are made alkaline with  $KOH$ , sulphur is precipitated. On standing, or warming, the precipitate disappears. The reaction is sensitive.<sup>20</sup>

(c) Nitron sulphate yields in concentrated test drops at first oily drops. Soon sheaves and radiating clumps of fine needles appear (Fig. 215, page 359). These crystals resemble those of nitron nitrate (Fig. 195, page 325) but are much more soluble. Nitron pentathionate is the least soluble of the nitron thionates; hence  $S_2O_5$ — can be detected in the presence of the other thionates, for it separates before any of the others and has a very different appearance.

(d) Benzyl-pseudo-thiourea forms a complex with pentathionates having a habit indistinguishable from that of the tetrathionate, but is so much more soluble that an experienced analyst may be able to distinguish between the two complexes by “seeding” the preparation (Fig. 223, page 361).

(e) Nickel ethylenediamine nitrate — No visible reaction.

(f) Luteocobalt chloride added to moderately concentrated solutions yields thin four-sided plates and tablets with oblique ends, singly or in imperfect radiates (Fig. 218, page 359). The test drops super-saturate and require “seeding.”

#### Notes on the Detection of the Poluthionates.

##### 1. With nitron sulphate.

In concentrated solutions the following interfere — nitrates, nitrites, chlorates, perchlorates, orthophosphates, iodides, chromates, bichromates, ferri- and ferro-cyanides, oxalates, tartrates.

In dilute solutions, nitrates, iodides, bichromates.

##### 2. With benzyl-pseudo-thiourea. (See Appendix, page 423.)

The following interfere — cyanides, ferri- and ferro-cyanides, chromates, bichromates, permanganates, carbonates, fluorides, hypochlorites, perchlorates, molybdates, tungstates, vanadates.

##### 3. With nickel ethylenediamine nitrate. (See Appendix, page 424.)

<sup>19</sup> *Jour. Chem. Soc.* 123, 1279 (1923).

<sup>20</sup> Foerster and Vogel: *Zeit. anorg. Chem.* 155, 161 (1926).

The following interfere — arsenates, permanganates, persulphates, iodates, sulphides, molybdates, tungstates.

4. With luteocobalt chloride.

The following interfere — persulphates, sulphates, pyrophosphates, molybdates, tungstates.

It will be obvious that the majority of the interferences are those of salts whose presence causes the almost immediate destruction of polythionates; the others interfere when present in great excess.

**Scheme for the Identification of the Anions of the Sulphur Group<sup>21</sup>**

I. *To a drop of a dilute solution of the unknown, which should be free from free alkali or acid, add a drop of silver nitrate solution.*

A. *No precipitate is obtained.*  $\text{SO}_4^{--}$ ;  $\text{S}_2\text{O}_6^{--}$ ;  $\text{S}_2\text{O}_8^{--}$ .

(a) Repeat, using a more concentrated drop.

$\text{S}_2\text{O}_6^{--}$  will not yield a precipitate.

$\text{SO}_4^{--}$  and  $\text{S}_2\text{O}_8^{--}$  will yield characteristic prisms.

Confirm with calcium acetate.

(b) If no precipitate was obtained in concentrated test drops, test for  $\text{S}_2\text{O}_6^{--}$ , using luteocobalt chloride.

Confirm with nickel ethylenediamine nitrate.

B. *A precipitate is obtained.*

$\text{S}^{--}$ ;  $\text{SO}_3^{--}$ ;  $\text{SO}_4^{--}$ ;  $\text{S}_2\text{O}_8^{--}$ ;  $\text{S}_2\text{O}_3^{--}$ ;  $\text{S}_3\text{O}_6^{--}$ ;  $\text{S}_4\text{O}_6^{--}$ ;  $\text{S}_5\text{O}_6^{--}$ .

(a) The precipitate is colorless and crystalline.

$\text{SO}_4^{--}$ ;  $\text{S}_2\text{O}_8^{--}$ .

(b) The precipitate is colorless but appears to be "amorphous" and is readily soluble in  $\text{HNO}_3$ ..... $\text{SO}_3^{--}$ .

(c) The precipitate is colored.

$\text{S}^{--}$ ;  $\text{S}_2\text{O}_8^{--}$ ;  $\text{S}_2\text{O}_3^{--}$ ;  $\text{S}_3\text{O}_6^{--}$ ;  $\text{S}_4\text{O}_6^{--}$ ;  $\text{S}_5\text{O}_6^{--}$ .

II. *To a drop of the solution of the unknown as in I, add a drop of a concentrated solution of luteocobalt chloride.*

A. Acicular crystals are formed ..... $\text{S}_2\text{O}_3^{--}$

B. Highly refractive tabular crystals ..... $\text{S}_3\text{O}_6^{--}$ ;  $\text{S}_5\text{O}_6^{--}$

C. No crystals separate ..... $\text{S}_4\text{O}_6^{--}$ ;  $\text{S}^{--}$

III. *To a drop of a neutral solution of the unknown, add a drop of a dilute solution of mercurous nitrate.*

A. A black precipitate is obtained ..... $\text{S}_2\text{O}_3^{--}$ ;  $\text{S}_3\text{O}_6^{--}$

<sup>21</sup> Chamot and Brickenkamp: *Mikrochemie* 16, 121 (1934).

- (a) Test a fresh portion with nickel ethylenedi-  
amine nitrate, if sheaves and radiates of fine  
needles result .....  $\text{S}_2\text{O}_3^{--}$
- (b) Test a fresh portion with benzyl  $\psi$  thiourea.  
Prisms and tablets indicate .....  $\text{S}_3\text{O}_6^{--}$
- B. A yellow precipitate separates .....  $\text{S}_4\text{O}_6^{--}$ ;  $\text{S}_5\text{O}_6^{--}$
- (a) Test a fresh portion with KOH or  
ammoniacal  $\text{AgNO}_3$ .  
If a precipitate is obtained .....  $\text{S}_5\text{O}_6^{--}$   
No precipitate .....  $\text{S}_4\text{O}_6^{--}$
- C. White or colorless acicular crystals separate  
in concentrated but not in very dilute test drops  $\text{SO}_4^{--}$ ;  $\text{S}_2\text{O}_8^{--}$
- D. A white precipitate is formed which rapidly  
changes to black .....  $\text{SO}_3^{--}$

**Selenates —  $\text{SeO}_4^{--}$ .** — Selenates are grouped here under the sulphur acids because of their close resemblance to sulphates and because of the large number of simple and double selenates that are known. Most of these selenates are isomorphous with the sulphates of the same metal.

The detection of  $\text{SeO}_4^{--}$  turns upon the identification of selenium in the compound (see Selenium, page 255) and upon observations of the close similarity in the behavior of  $\text{SeO}_4^{--}$  and  $\text{SO}_4^{--}$  to reagents. Although the common salts of  $\text{SeO}_4^{--}$  separate from test drops in crystal forms closely resembling each other, the experienced analyst can often distinguish slight differences in the character of the crystals sufficient to lead him to suspect the presence of selenates in the material he may have under examination; but it is usually necessary for him to test drops of varying concentration. In the outline given below these minor differences have been somewhat overemphasized.

For any given cation the refractive indices of its selenates are decidedly higher than those of its sulphates, the differences being sufficiently great to warrant rough observations by the Immersion Method (*Vol. I*, page 360) and thus quickly ascertain whether the salt in question is preponderatingly selenate or sulphate.

(a) *Group Reactions.*

1.  $\text{AgNO}_3$  produces at once a very dense, heavy, white granular precipitate. In test drops of approximately like concentration of  $\text{SeO}_4^{--}$  and of  $\text{SO}_4^{--}$  the separation of  $\text{Ag}_2\text{SeO}_4$  is more rapid and denser than that of  $\text{Ag}_2\text{SO}_4$ . This difference in the rates of separation is of no analytical value since silver sulphate and silver selenate are isomorphous.

The crystals of  $\text{Ag}_2\text{SeO}_4$  do not develop into well-formed tablets, plates, and rhombs as readily as those of  $\text{Ag}_2\text{SO}_4$ , but remain smaller, more irregular, and more dendritic. The rhombs usually "sprout" at the acute ends, becoming rough acicular dendrites with rhombiform central outline. They are highly refractive and scatter light more strongly than crystals of  $\text{Ag}_2\text{SO}_4$ .

2.  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives a white granular precipitate somewhat less quickly formed than that with  $\text{SO}_4^{--}$ , but on the other hand readily developing into much larger crystalline grains. These grains are generally thicker than those formed by  $\text{BaSO}_4$ , and have an hour-glass shape. Most of them are colorless; others are sufficiently drusy to scatter light and appear white, or, by transmitted light, black. Colorless lenticular grains also abound. The chief difference between  $\text{BaSeO}_4$  and  $\text{BaSO}_4$  as formed in test drops is that  $\text{BaSeO}_4$  separates more slowly and forms larger and thicker crystalline grains.

3. With  $\text{Ti}(\text{C}_2\text{H}_3\text{O}_2)_2$  no immediate separation of crystals occurs, but on standing long slender prisms appear and many extraordinarily fine, hair-like crystals occur singly, rarely in groups or masses (Fig. 206, page 341). Although long, they are less prone to bend and curve than most trichiten crystals generally are. When the prisms grow thick they are not distinguishable from those of  $\text{Ti}_2\text{SO}_4$  (Figs. 204, 205, page 341).

$\text{TiSeO}_4$  crystals are characterized by their high refractive power and strong birefringence with parallel extinction. The great majority of the crystals are longer and slenderer than those of  $\text{Ti}_2\text{SO}_3$  and have terminal angles less well developed. It is best to allow the preparation to pass almost to dryness.

4. With  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  no distinct crystals are obtained even when the test drop goes to dryness; the dry film shows only irregular rosettes of very low refractive index, not differing materially from the crystals of the reagent.

5.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  precipitates at once, from even very dilute solutions, a snow-white, dense, "amorphous" mass, soon changing into very minute granular crystals, and eventually developing into crystalline grains and very short rods with rounded ends. The crystals always remain small, and require a magnification of about  $200\times$  for their resolution.

**Selenites —  $\text{SeO}_3^{--}$ .** — The selenites are, for the most part, unstable salts corresponding to the sulphites. Although the probability of the analyst having to test for the presence of selenites is very remote, a brief résumé of the group reactions of  $\text{SeO}_3^{--}$  is nevertheless given.

As in the case of selenates, the first step is the detection of selenium.

*(a) Group Reactions.*

1.  $\text{AgNO}_3$  gives in very dilute solutions a dense white precipitate consisting of tiny grains and short acicular crystals in crosses and irregular groups. On standing a short time, these acicular crystals become rough and bristling, and develop into long dendrites with one end spreading out into thin leaf-like or fern-like masses. The body of these long dendrites bristles with tiny angular crystals, growing parallel with each other at very acute angles with the directions of elongation of the acicular dendrites.

2.  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives no reaction at first, and no crystals appear until evaporation has taken place; then around the circumference of the test drop disks appear. These disks are made up of fine needles. As the concentration of the drop rises through further evaporation, the disks grow fan-shaped and irregular.

3.  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives a reaction strictly analogous to that obtained with  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ , but the calcium salt is more soluble than that of barium and no crystals appear until the test drop has evaporated almost to dryness; then tiny disks, made up of exceedingly minute needles, form at the circumference of the test drop. These disks are much less refractive than those obtained with barium, and retain their circular form when the drop goes dry.

4.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  produces a white "amorphous" precipitate, becoming granular and then distinctly crystalline in a zone around the granular deposit. Under a magnification of about  $200\times$  the crystals are seen to consist of tiny dendritic aggregates or dendritic skeletons of very variable form.

5. With  $\text{Ti}(\text{C}_2\text{H}_3\text{O}_2)_2$  no precipitate is produced even in very concentrated solutions. As the test drop passes to dryness, merely a crystalline crust is obtained at the circumference of the drop.

**DETECTION OF THE ANIONS OF THE CHROMIUM GROUP**

Chromates and bichromates are usually yellow or red salts, yielding yellow or red solutions. The bichromates are, as a rule, deeper in color than the chromates.

Chromates of the alkali group, and those of Mg, Ca, Zn, Cd, Cu, are readily soluble in water. Those of Sr,  $\text{Hg}^{++}$ , only slightly soluble; those of Ba, Bi, Mn,  $\text{Hg}^+$ , Ag, Pb are practically insoluble.

Bichromates of Ag, Pb,  $\text{Hg}^+$  are practically insoluble in water.

Insoluble chromates fused with KOH yield soluble  $\text{K}_2\text{CrO}_4$ . Many bichromates are unstable and are decomposed by water. Basic, double, and polychromates are not infrequently met with.

Of the molybdates commonly encountered those of the alkali metals alone are easily soluble in water. Solutions of the alkali molybdates therefore give with solutions of the salts of other metals a precipitate of insoluble (or very difficultly soluble) molybdates.

Di- and tri-molybdates are known and are more soluble than the normal molybdates. Molybdates enter into the formation of many complex ions whose true natures have not yet been definitely established. Fortunately the analyst seldom has to deal with molybdates other than the alkali molybdates.

Dilute nitric acid added to a test drop containing a molybdate precipitates  $\text{MoO}_3$ , soluble in slight excess of the acid.

Closely related to the molybdates are the tungstates, of which the orthotungstates derived from the acid  $\text{H}_2\text{WO}_4$  and the metatungstates derived from the acid  $\text{H}_2\text{W}_4\text{O}_{13}$  are the best known. The paratungstates  $\text{R}_{10}\text{W}_{12}\text{O}_{41} \cdot x\text{H}_2\text{O}$  are rare, and for the most part insoluble in water. Even the alkali paratungstates are only very slightly soluble in water.

The alkali orthotungstates are readily soluble in water, but most other orthotungstates are insoluble or nearly so. Most metatungstates are water-soluble.

The composition of tungstates varies greatly according to the conditions under which they are formed.

Soluble orthotungstates can be differentiated from soluble orthomolybdates by means of dilute  $\text{HNO}_3$  added to the test drop by Method I. As stated above, the  $\text{MoO}_3$  at first formed is soluble in excess of the reagent, but the white hydrated  $\text{WO}_3$  precipitated by  $\text{HNO}_3$  is insoluble in excess.

$\text{HNO}_3$  added (by Method I) to a test drop containing meta- or paratungstates causes no precipitate.

The water-soluble tungstates are white (colorless).

### Chromates — $\text{CrO}_4^{--}$ .

#### (a) *Group Reactions.*

1. With  $\text{AgNO}_3$  there is first formed a heavy, dark red, "amorphous" precipitate of  $\text{Ag}_2\text{CrO}_4$ . On standing there are formed, in the zone beyond the precipitate, slender needles, small irregular platelets, and tiny, acute, rhomb-shaped dark red plates. There are also irregular plates and scales in a great variety of forms. The solubility of  $\text{Ag}_2\text{CrO}_4$  is so low that the crystals are not well developed. The value of recrystallizing, or precipitating  $\text{Ag}_2\text{CrO}_4$  in the presence of  $\text{Ag}_2\text{SO}_4$ , with the formation of an isomorphous mixture of these two salts, has already been referred to, and is especially important when testing for

$\text{CrO}_4^{--}$ . (See Chromium, page 244; Silver, page 280; Fig. 210, page 355; Fig. 203, page 341.)

2.  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  yields a fine granular precipitate, faintly yellow in color, and slowly becoming crystalline. The crystallization is most marked in the outer zone. Tiny, irregular crystalline masses of variable outline are formed, together with tiny clumps of dendrites made up of rough needles. Some of these needles form radiates.

The insolubility of barium chromate provides a means of separating  $\text{CrO}_4^{--}$  from other anions in mixtures which would be difficult of analysis were not  $\text{CrO}_4^{--}$  removed.

3. With  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  there is no precipitate, and no separation of crystals takes place on standing.

4.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  produces, at once, a heavy, bright yellow, gelatinous precipitate that undergoes no change on standing.

5.  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$  yields a bright yellow, gelatinous precipitate like that obtained with  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , but on standing the precipitate becomes granular and slow crystallization takes place with the formation of groups and tufts of fine needles and mossy radiates.

*(b) Reaction with Manganese.*

$\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2$  produces at once a dark brown, "amorphous" precipitate, slowly becoming crystalline in part. In the outer zone tufts and clumps of very fine short needles appear, followed by radiates and bristling, very dark brown, opaque masses. The size of the needles and the character of their grouping varies with the concentration (Fig. 163, page 239).

With  $\text{MnSO}_4$  no precipitate is at first formed, but on standing moderately large radiates of pleochroic needles separate. Sheaves and irregular tufts are also formed.

The reaction with manganese salts affords a ready method for differentiating between  $\text{CrO}_4^{--}$  and  $\text{Cr}_2\text{O}_7^{--}$ , for with the latter no crystals are obtained.

The test should be performed in strictly neutral or slightly alkaline solutions.

**Bichromates —  $\text{Cr}_2\text{O}_7^{--}$ .**

*(a) Group Reactions.*

1.  $\text{AgNO}_3$  added by Method I to the "neutral" test drop gives an instantaneous, dark red precipitate, crystallizing almost immediately in slender dichroic prisms, thin plates, and rectangular tablets; many large but thin, irregular scales are also formed.

2.  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  yields a granular precipitate in which no definite crystal forms can be observed. Although  $\text{BaCrO}_4$  is formed, it does not crystallize as well as when precipitated by  $\text{CrO}_4^{--}$

3.  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives no precipitate, and no crystals separate on standing.

4.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives  $\text{PbCrO}_4$  as a bright yellow, gelatinous mass, undergoing no change in standing.

5. With  $\text{Ti}(\text{C}_2\text{H}_3\text{O}_2)_2$  a yellow and an orange precipitate is obtained, at first "amorphous," later becoming granular. Crystallization takes place less readily than in the case of  $\text{CrO}_4^{--}$ .

(b)  $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives no precipitate and there is no separation of crystals (distinction from  $\text{CrO}_4^{--}$ ), but as the test drop passes to dryness a few tiny, very dark brown (practically black), more or less spherical granules appear in little patches at the circumference of the drop and finally a ring of dark brown colloidal material is formed around the circumference of the test drop.

When  $\text{MnSO}_4$  is employed instead of the acetate, no precipitate, no separation of crystals or granules, and no brown ring is obtained.

(c) The reaction of mercurous salts toward  $\text{Cr}_2\text{O}_7^{--}$  ions in  $\text{HNO}_3$  solution has been discussed under Mercury, page 161. It is, however, difficult so to adjust the condition as to obtain characteristic crystals of the mercurous salt, and the test can be regarded in the light of a confirmatory test only (Fig. 110, page 151).

### Molybdates — $(\text{MoO}_4)^{--}$ ?

There is probably little justification for thus indicating the anion of molybdates save that of brevity and convenience. Simple molybdate salts exist in alkaline solutions only. Most molybdates are complex compounds composed of salts of polymerized  $\text{H}_2\text{MoO}_4$ , plus simple salts of the unpolymerized acid, plus hydrated oxides of Mo. A good example is that of the common reagent ammonium molybdate (ammonium paramolybdate) for which a multitude of different formulas are in current use.

In microscopical qualitative analysis of material of unknown nature we can do little more than ascertain that the material contains Mo (see page 248) ; that the Mo is, or is not, probably a component of the acidic part of the salt or bound up in a heteropoly complex. The true nature of the compound can rarely be definitely established without recourse to quantitative data.

The few reactions for "molybdates" given below cannot be strictly correct because of the complex nature of practically all commercially produced molybdates, which vary with methods of manufacture, storage, and age: *Caveat emptor*.

#### (a) Group Reactions.

1. With  $\text{AgNO}_3$  by Method I a yellow "amorphous" precipitate is produced.



2.  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  yields a white, thick, heavy "amorphous" precipitate with a tendency to become granular. No definite crystals can be discerned.

3. With  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  a fine, white, granular precipitate is obtained, and on standing tiny, colorless disks appear which require a magnification of 200 to 300 $\times$  for their resolution.

4.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  yields a heavy, white gelatinous or curdy precipitate, undergoing no perceptible change on standing.

5. With  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$  there is first obtained a white, granular, almost "amorphous" precipitate. In a few seconds crystallization in the outer zone takes place and small colorless hexagonal plates and tablets appear; at the same time large dendritic masses composed of irregular hexagons are formed upon the granular precipitate. As the test drop passes to dryness it becomes filled with irregular scales and imperfect hexagons (Fig. 160, page 239).

$(\text{WO}_4^-)$ ? gives a similar reaction, but thallos tungstate is slightly less soluble than thallos molybdate and hence the hexagons are not apt to be so well developed under like concentrations (Fig. 161, page 239). These two salts appear to be isomorphous.

6. Dissolve the material in hot nitric acid. Evaporate to dryness. Dissolve the residue in hydrochloric and again evaporate to dryness. Molybdates yield a green or blue oxide; tungstates a yellow oxide. Moisten the residue with a drop or two of hydrogen peroxide; the blue color of the molybdenum oxide is intensified (Staples).

(b) *Reaction with Phosphates.*

To the test drop, add by Method I a solution of  $\text{H}_2\text{NH}_4\text{PO}_4$ , acidified with  $\text{HNO}_3$ . Warm *gently*. A fine, granular, bright yellow precipitate developing into crystalline granules is obtained. (See  $\text{PO}_4^-$ , page 339. Fig. 164, page 251.) Under proper conditions  $(\text{WO}_4^-)$ ? may give an analogous reaction, but the precipitate is practically colorless.

When the reagent flows into the test drop, the  $\text{HNO}_3$  usually first precipitates white hydrous  $\text{MoO}_3$  or  $\text{WO}_3$ . The  $\text{MoO}_3$  dissolves in the excess of acid, and on warming the phospho-compound results; but because the heavy precipitate of  $\text{MoO}_3$  prevents a free flow of the acid into the test drop the precipitate obtained is usually partly  $\text{MoO}_3$ , white, and partly phosphomolybdate, yellow. Since hydrous  $\text{WO}_3$  is practically insoluble in  $\text{HNO}_3$ , the formation of a phosphotungstate is highly problematical, and when the preparation is heated the "amorphous"  $\text{WO}_3$  turns yellow. The change from the white compound to the yellow requires a temperature almost to the boiling point. It is therefore highly important that in this test the preparation shall never be more than *very gently warmed*. A further precaution is essential: a test drop

must always be tested with dilute  $\text{HNO}_3$  before the phosphate-nitric acid reagent is employed, in order to ascertain whether a precipitate is produced by the acid alone.

Since sodium phosphomolybdate is quite soluble, materials containing a large amount of sodium salts or consisting of  $\text{Na}_2\text{MoO}_4$  rarely yield a decisive test unless repeatedly heated and the preparation is brought almost to dryness.

It has been pointed out<sup>22</sup> that the reason the phosphomolybdate test frequently is unsatisfactory is that insoluble oxides are formed by the added acid. Dissolve in ammonium hydroxide and reprecipitate with  $\text{HNO}_3$ .

**Tungstates** —  $(\text{WO}_4^-)?$ ;  $(\text{W}_4\text{O}_{13}^-)$ ,  $(\text{W}_{12}\text{O}_{41}^-)$ .

(a) *Group Reactions.*

1. With  $\text{AgNO}_3$  orthotungstates yield a heavy, cream-colored, "amorphous" precipitate which undergoes no perceptible change on standing. A similar precipitate is obtained with metatungstates, but in a short time squares and rhombs appear, growing into small, colorless, highly refractive octahedra; at first most of the octahedra are malformed, but they soon fill out, and, as the test drop passes to dryness, well-formed crystals separate in large numbers. Paratungstates give no crystals.

2. With  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  orthotungstates give a granular precipitate, changing in part to colorless, drusy, very tiny, lenticular grains, grouping themselves into spreading irregular aggregates. Meta compounds yield "amorphous" precipitates becoming granular, and under favorable conditions a few tiny disks are formed. No recognizable reaction is obtained with paratungstates.

3. With  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  no definite crystals are obtainable. On standing, a few colorless tiny disks are obtained with orthotungstates, but nothing with meta- or para-tungstates.

4.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives gelatinous or somewhat granular precipitates with all tungstates, but no crystals separate.

5. With orthotungstates  $\text{Ti}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives hexagonal plates and tablets similar in appearance to those obtained with orthomolybdates, but in the case of  $(\text{WO}_4^-)?$  there is a greater tendency to produce skeleton crystals (stars and rosettes). (Fig. 161, page 239.) No hexagons are obtained with meta- or para-tungstates, and no definite crystals; an "amorphous" or granular precipitate only is obtainable.

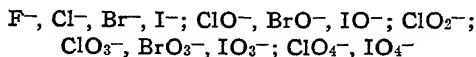
(b) Tested with a soluble phosphate in  $\text{HNO}_3$  solution, tungstates give a white "amorphous" or granular precipitate, which may develop

<sup>22</sup> Staples: *Amer. Mineralogist*, *loc. cit.*

into tiny colorless disks. A bright yellow precipitate is never obtained, nor are crystals formed of definite shape.

Sodium salts prevent the precipitation of ammonium phosphotungstates, but do not interfere with the precipitation of hydrous  $\text{WO}_3$  by  $\text{HNO}_3$ .

#### DETECTION OF THE ANIONS OF THE HALOGEN GROUP<sup>23</sup>



Although the halogens present many striking relationships to the chemist, these same family resemblances are likely to be rather serious obstacles in the development of microscopical tests for their identification. Most microscopical tests involve the formation of a crystal form or habit, typical and characteristic of the substance sought. In the case of the compounds of the halogens, their close relationship according to their positions in the Periodic System manifests itself in a high degree of isomorphism of their crystalline compounds, and, for this reason, similar salts are likely to be very much alike, not only in their crystalline character but also in their physical and chemical properties.

As a preliminary step in an analysis the authors have found nothing superior to the grouping offered by the Bunsen-Treadwell classification based upon the formation and properties of the silver (or barium) salts of the halogens, as already outlined (page 316). According to this classification the silver salts of the anions fall into one of three groups.

1. Silver salts insoluble in water and insoluble in strong nitric acid.
2. Silver salts insoluble in water but soluble in  $\text{HNO}_3$ .
3. Silver salts soluble in water.

In the discussion which follows, unless otherwise stated, it is understood that when a substance of unknown composition is found to fall in one of the groups 1, 2, or 3, identity tests are to be made on *separate* portions of the original material, the grouping serving merely as a time-saving device.

The corresponding compounds of the halogens may best be considered together at first, as a means of illustrating their similarities and emphasizing what differences exist.

**Halides** —  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ . — With the exception of fluorides, the gradation in the chemical and physical properties of the various halides

<sup>23</sup> Mason: *Mikrochemie* 4, 145-148 (1926).

Chamot and Mason: *idem.* 5, 85-101 (1927); 6, 82-91 (1928).

is so perfect that the differences between them are more likely to be those of degree, rather than of kind. The isomorphism of their crystals is particularly striking, and, as a consequence, little help is to be expected from tests depending on differences of crystal habit of different halides of the same metal. Silver chloride, bromide, and iodide are isomorphous, and are similar in crystallization. Their solubilities do not differ widely enough so that any dependable separation may be obtained by taking advantage of this property. In the case of some other metals, however, the solubilities of their halides differ more greatly, and distinctions may be based on this.

(a) *Group Reactions.*

1.  $\text{AgNO}_3$  gives no precipitate with fluorides. With  $\text{Cl}^-$  very fine-grained crystals, which develop into visible octahedra on standing, are obtained from solutions containing  $> 0.5 \mu\text{g. Cl}$  per drop. (See Fig. 211, page 355.)  $\text{Br}^-$  yields much finer crystals, the form of which is rarely recognizable from solutions of concentrations similar to the above.  $\text{I}^-$  gives a precipitate too fine for its form to be recognized, with a limit of about  $0.02 \mu\text{g. of I}^-$  per drop.  $\text{AgCl}$  and  $\text{AgBr}$  may be recrystallized from  $\text{NH}_4\text{OH}$  solution, yielding more distinct octahedra, but their solubilities are not different enough to permit a separation by means of this solvent, nor even an indication as to whether the precipitate consists mainly of  $\text{AgCl}$  or  $\text{AgBr}$ .  $\text{AgI}$  is not sufficiently soluble in  $\text{NH}_4\text{OH}$  solution for recrystallization to take place, and the other silver halides may be extracted from it practically completely.

2.  $\text{TiNO}_3$  gives with  $\text{Cl}^-$ , in concentrations  $> 15 \mu\text{g. per drop}$ , highly refractive isotropic octahedra, cubes, stars, and crosses, which are soluble in hot water and recrystallize from it as coarse cubes. (See Fig. 121, page 183.)  $\text{Br}^-$  behaves similarly, in concentrations  $> 2 \mu\text{g. per drop}$ ; the crystals of  $\text{TiCl}$  and  $\text{TiBr}$  are so similar that the variations of habit ordinarily observed may be due as much to differences in concentration as to the presence of different anions.  $\text{TiI}$  is very much less soluble than the chloride or bromide, and precipitates as very minute cubes from solutions containing  $> 0.4 \mu\text{g. I}^-$  per drop. This fine-grained precipitate may sometimes enable iodides to be distinguished from chlorides and bromides.

3.  $\text{Pb}(\text{NO}_3)_2$  or  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  gives crystals with either  $\text{Cl}^-$  or  $\text{Br}^-$  ( $> 100 \mu\text{g. per drop}$ ), which are highly refractive, flat, orthorhombic prisms, frequently having forked or pointed ends or showing skeleton markings on their faces (see Figs. 124, 125, page 183). Their solubility is appreciable, and they are readily recrystallized from hot water. With  $\text{I}^-$  distinctive crystals are obtained, in the form of thin, yellow, hexagonal plates (see Fig. 138, page 205). From very dilute solutions

only a very fine-grained precipitate may be formed, but its color and iridescent or scintillating appearance by reflected light is characteristic.  $\text{PbI}_2$  is a useful test for iodides in mixtures with the other halides, though of limited sensitivity ( $10\text{--}20\text{ }\mu\text{g. I}^-$  per drop).

4. Mercuric salts give a fine-grained, red precipitate of  $\text{HgI}_2$ , the limit being about that of the  $\text{PbI}_2$  test. (See page 158.)  $\text{Cl}^-$  and  $\text{Br}^-$  give precipitates only from concentrated solutions.

5.  $\text{CuSO}_4$  gives a fine-grained, yellowish precipitate of  $\text{CuI}$ , having about the above limit of sensitivity. (See page 159.)  $\text{Cl}^-$  and  $\text{Br}^-$  give no precipitates.

6.  $\text{PdCl}_2$  yields a dark brown or black, very fine-grained precipitate with concentrations of  $\text{I}^- > 0.7\text{ }\mu\text{g.}$  per drop. (See page 292.)

(b) *Oxidation to the Free Halogen.*

Differential oxidation of  $\text{I}^-$  to  $\text{I}_2$ , or  $\text{Br}^-$  to  $\text{Br}_2$ , without affecting the other halides present, is not possible without more precise control than is practicable on a micro scale. However,  $\text{I}^-$  and  $\text{Br}^-$  can be oxidized together in mixtures and the evolved  $\text{I}_2$  or  $\text{Br}_2$  identified. For this purpose  $\text{KNO}_2$  or  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , in acid solution, are suitable if the liberated  $\text{I}_2$  is to be tested by starch in the same drop. If the oxidation is carried out in a micro crucible (page 17) as is necessary when  $\text{Br}^-$  is present alone or in mixture with  $\text{I}^-$  or  $\text{Cl}^-$ , other oxidizing agents, such as  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{CrO}_3$ , or  $\text{KMnO}_4$  in acid solution, or even less powerful oxidants may be employed.

By removal of  $\text{I}^-$  and  $\text{Br}^-$  from mixtures of halides,  $\text{Cl}^-$  may be tested for with greater certainty than if these anions were present. Oxidation by boiling cautiously two or three minutes with 10 per cent (by volume)  $\text{HNO}_3$  in a micro crucible, until negative tests for  $\text{Br}_2$  and  $\text{I}_2$  are obtained, will leave  $\text{Cl}^-$  unchanged. The acid solution remaining may be tested for  $\text{Cl}^-$  with  $\text{AgNO}_3$ . About one per cent of  $\text{Cl}^-$  in mixture with the other halides may be recognized by this procedure.

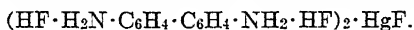
(c) *Specific Tests for Individual Halides.*

**Fluorine** is distinctly different from the other halogens as regards its compounds and reactions, so that its analytical detection cannot be based on group reactions such as those discussed above. Fluorides may be recognized by their exceptionally low refractive indices and by the possibility of  $\text{HF}$  being liberated by a strong acid such as  $\text{H}_2\text{SO}_4$ . The etching action of  $\text{HF}$  on glass may be used for identification, but more positive evidence is offered by the formation of fluosilicates of characteristic crystalline nature. (See Fig. 37, page 61.)

For the detection of fluorine in insoluble materials such as silicates, etc., the material should be first fused with  $\text{Na}_2\text{CO}_3$ , the melt dissolved in boiling water, precipitated with  $(\text{NH}_4)_2\text{CO}_3$ , filtered, to the filtrate a little  $\text{NH}_4\text{Cl}$  added, and the

clear solution made just neutral with HCl. The fluorine can then be precipitated with  $\text{CaCl}_2$ , centrifuged, and the precipitate thus obtained tested for F by etching and fluosilicate tests.

According to Pertusi,<sup>24</sup> alkali fluorides yield a characteristic yellow, crystalline precipitate with benzidine acetate and mercuric acetate in concentrated acetic acid. A more sensitive reaction is obtained if mercuric succinimide is employed; the reaction product in this case is believed to have the composition



**Chlorides** are indicated, but not identified, by their crystalline precipitates with  $\text{Ag}^+$ ,  $\text{Ti}^+$ , or  $\text{Pb}^{++}$ . Bromides, and preferably also iodides, must first be eliminated (by boiling with 10 per cent  $\text{HNO}_3$ ) if these precipitates are to be ascribed to  $\text{Cl}^-$ . Since some  $\text{Cl}^-$  is almost always likely to be present with the other halides, a distinct test is more important than a faint one which might be due to traces of unremoved  $\text{Br}^-$  or  $\text{I}^-$ .

(1) *Chromyl Chloride Reaction.*

The well-known chromyl chloride reaction may be carried out on a micro scale, and will serve to reveal the presence of any combined chlorine in the sample; it does not serve to differentiate between  $\text{Cl}^-$ ,  $\text{ClO}_3^-$ , and  $\text{ClO}_4^-$ , however.

The unknown material, in solid form, is added to a hot mixture of chromic anhydride  $\text{CrO}_3$  (or  $\text{K}_2\text{Cr}_2\text{O}_7$ ) and concentrated  $\text{H}_2\text{SO}_4$  in a micro crucible. If a compound of chlorine is present,  $\text{CrO}_2\text{Cl}_2$  will be formed, and this will be volatilized (b.p.  $115^\circ$ ) and may be "fixed" in a small drop of  $\text{NH}_4\text{OH}$  on the under surface of the cover-slide. Since the  $\text{CrO}_2\text{Cl}_2$  vapor is heavy, it is well to allow a minute or two for it to diffuse into the test drop, or *cautious* heating may be employed; tilting or rocking the crucible will aid the diffusion. The least spattering renders the test useless, for the  $\text{H}_2\text{CrO}_4$  in the test drop will give the same reactions as would  $\text{CrO}_2\text{Cl}_2$ .  $\text{SO}_3$  is also evolved, as are  $\text{Br}_2$  and  $\text{I}_2$  if  $\text{Br}^-$  and  $\text{I}^-$  were present. The presence of  $\text{CrO}_4^{--}$  in the test drop, *provided no spattering has occurred*, indicates that  $\text{CrO}_2\text{Cl}_2$  has been formed, which must have come from a chlorine compound.

If an excess of solid  $\text{AgNO}_3$  is added to the neutral or acid test drop, containing  $\text{CrO}_2\text{Cl}_2$  (or rather  $\text{H}_2\text{CrO}_4$  and  $\text{HCl}$ , from interaction with water),  $\text{AgCl}$  (white) is first precipitated and when the precipitation of the chloride is complete the more soluble  $\text{Ag}_2\text{CrO}_4$  separates as an orange to red precipitate, the color of which is readily observed against the white  $\text{AgCl}$ . Any  $\text{Ag}_2\text{SO}_4$  formed by the action of the  $\text{SO}_3$  will be colorless; any  $\text{Br}_2$  or  $\text{I}_2$  from the  $\text{Br}^-$  or  $\text{I}^-$  will be precipitated as  $\text{AgBr}$  or  $\text{AgI}$ . The only highly colored precipitate is the  $\text{Ag}_2\text{CrO}_4$ . The

<sup>24</sup> *Atti III Congr. naz. chim. pura applicata* 1929, 537.

identification of the  $\text{Ag}_2\text{CrO}_4$  may be confirmed by recrystallization from  $\text{NH}_4\text{OH}$ . If the test drop is made strongly ammoniacal, all the precipitate (except  $\text{AgI}$ ) will dissolve, and on exposure to the air the silver salts will be reprecipitated in more definite crystalline form. Silver halides will be formed first, in various modifications of the octahedron;  $\text{Ag}_2\text{SO}_4$  and  $\text{Ag}_2\text{CrO}_4$ , being isomorphous, will occur as mixed crystals, colored according to the proportion of  $\text{Ag}_2\text{CrO}_4$  present. These may range from orange to deep red, and according to the intensity of the color exhibit pleochroism (red to orange). These crystals of  $\text{Ag}_2(\text{Cr},\text{S})\text{O}_4$  may occur as short orthorhombic prisms with pointed ends, as rhombs, or as dendritic and leaf-shaped forms, appearing first at the edges of the drop.

During the exposure of the  $\text{NH}_4\text{OH}$  test drop to the vapors from the crucible, the under surface of the slide should be watched carefully, so that if spattering occurs it may be observed and the drop discarded. It is well to examine the slide under the microscope also, to see if any yellow droplets of the chromic acid mixture have spattered up on its surface. If these precautions are taken, the  $\text{CrO}_2\text{Cl}_2$  test is reasonably dependable, and its execution on a micro scale is only a matter of a few minutes.  $\text{F}^-$  ions must be absent.

In the presence of much  $\text{Br}^-$  or  $\text{I}^-$ , the test is best modified by oxidizing the bulk of the  $\text{Br}^-$  or  $\text{I}^-$  with  $\text{H}_2\text{CrO}_4$  and *dilute*  $\text{H}_2\text{SO}_4$  (1 : 4) first; little if any  $\text{Cl}^-$  is lost under these conditions. The heating during this oxidation serves to concentrate the  $\text{H}_2\text{SO}_4$ , and an excess of  $\text{CrO}_3$  and of concentrated  $\text{H}_2\text{SO}_4$  is added to furnish the proper conditions for the formation of  $\text{CrO}_2\text{Cl}_2$ , which is then driven off by gentle heating, and tested for as above. For critical work it is well to run a blank, to test out the  $\text{H}_2\text{SO}_4$ , etc., employed and, in any case, one should consider only a distinct orange to red color of the crystals in the test drop as a positive test. The sensitivity of the  $\text{CrO}_2\text{Cl}_2$  test is such that about 3  $\mu\text{g}$ . of chlorine may be detected, but the presence of excessive amounts of  $\text{Br}^-$  or  $\text{I}^-$  decreases the sensitivity.

**Bromides** are not to be distinguished from chlorides by the group reactions mentioned above. The identification of free  $\text{Br}_2$  is the most conclusive means of proving the presence of  $\text{Br}^-$ .

(1) *With Starch.*

$\text{Br}_2$  may be indicated in high concentrations ( $> 100 \mu\text{g}$ . per drop), by a yellow color with the starch used in testing for  $\text{I}_2$ , provided the latter is absent. (See page 378.)

(2) *With m-Phenylenediamine.*

A much more sensitive and reliable test depends on the formation of a

characteristic crystalline precipitate of 2,4,6-tribrom-phenylenediamine, when  $\text{Br}_2$  is brought in contact with a solution of *m*-phenylenediamine hydrochloride.<sup>25</sup>

The oxidation of  $\text{Br}^-$  to  $\text{Br}_2$  is carried out in a micro crucible, by means of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ , or  $\text{CrO}_3$ , in acid solution, or dilute  $\text{HNO}_3$ . (See page 375.)  $\text{Cl}^-$  and  $\text{I}^-$ , if present, are likewise oxidized to  $\text{Cl}_2$  and  $\text{I}_2$ . The *m*-phenylenediamine hydrochloride, in a solution about  $\frac{1}{10}$  saturated and to which a trace of  $\text{H}_2\text{SO}_4$  has been added, is exposed to the liberated halogens as a tiny drop on the under surface of the slide which covers the crucible.  $\text{Br}_2$  yields fine-grained crystals, if present in large amount, especially if the concentration of the reagent drop is high. When formed more slowly, or in an acidified solution of the reagent, the crystals are small fusiform needles, single and in clusters, highly refractive and strongly birefringent with parallel extinction (Fig. 212, page 355). Their formation may be observed through the slide without uncovering the crucible. Gentle warming is advantageous when small amounts of  $\text{Br}_2$  are evolved, but it must not be carried to the point of causing steam to condense on the slide.

$\text{Cl}_2$  and  $\text{I}_2$  give no such precipitate, though if present in large amount they may cause the formation of oily droplets which disappear on exposure to the air. An excess of  $\text{I}_2$  may be removed by gradual addition of the oxidizing agent, with little loss of  $\text{Br}_2$ ; the latter may be tested for during the evolution of the  $\text{I}_2$  and will appear only when the oxidation of  $\text{I}^-$  is nearly complete. The limit of sensitivity is about 0.5  $\mu\text{g}$ .  $\text{Br}^-$ , except in the presence of a large excess of  $\text{I}^-$ . In mixtures with  $\text{I}^-$ , as little as one part in 500 may be detected.

Aniline hydrochloride may be used as a substitute for *m*-phenylenediamine hydrochloride; it gives a somewhat similar precipitate with  $\text{Br}_2$  and none with the other halogen.

Iodides may be identified by means of the well-known coloration which free  $\text{I}_2$  gives with starch.

#### (1) Oxidation to Iodine.

The oxidation of  $\text{I}^-$  to  $\text{I}_2$  may be carried out in a drop of solution on an object slide.  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  is a satisfactory oxidizing agent;  $\text{KNO}_2$  is also suitable. To the solution to be tested, acidified with  $\text{H}_2\text{SO}_4$ , add a few granules of starch<sup>26</sup> and a fragment or two of the oxidizing agent. Very gentle heating will hasten the reaction. If  $\text{I}^-$  is present the grains of starch will become blue to violet, and may be

<sup>25</sup> Mason: *Mikrochemie* 4, 145-148 (1926).

<sup>26</sup> *Canna edulis*, arrowroot (maranta), or potato starches are more sensitive than others. Previous incipient gelatinization, by heat or by alkali, increases the delicacy of the test.



almost black if a large amount of  $I_2$  is set free. In such cases free iodine is sometimes visible as a yellow zone in the solution, or even as minute, acute, rhombic brown crystals. A large excess of an alkali iodide may cause the starch to be colored reddish or brownish hues. The sensitivity of this test for  $I^-$  is about  $0.8 \mu\text{g.}$  of iodine, which is beyond the concentration at which  $\text{Ag}^+$  gives a precipitate with  $I^-$ . The presence of other halides has little effect; one part of iodide in several thousand parts of bromides or chlorides can be detected.

(2) Distillation in a micro crucible affords a means of separating the liberated  $I_2$  from any substances in the unknown solution which might interfere with the "starch-iodide" test. The oxidation of  $I^-$  to  $I_2$  is carried out as in the case of  $\text{Br}^-$ . The above oxidizing agents may be used, or others such as  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{CrO}_3$ ,  $\text{PbO}_2$ , preferably in acid solution. Cautious heating aids in volatilizing the  $I_2$ , which comes in contact with a tiny drop of water containing a few granules of starch, on the under surface of the slide covering the micro crucible. The coloration of the starch may be followed without uncovering the crucible.

This modification of the test permits the identification of about  $1.5 \mu\text{g.}$  of  $I$ . The other halides decrease the sensitivity very little, unless present in large excess. It is desirable that the oxidizing agent should not liberate too much  $\text{Br}_2$  or  $\text{Cl}_2$ , or oxidation to  $\text{IO}_3^-$  may take place; for this reason  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $\text{KNO}_2$ , or  $\text{K}_2\text{Cr}_2\text{O}_7$  are preferable to stronger oxidizing agents such as  $\text{KMnO}_4$ .

(3) The specific oxidation tests for  $\text{Br}^-$  and  $I^-$  may be utilized to test for other halides. For example, if  $\text{KBr}$  and *m*-phenylenediamine are both present in the test drop and a strong oxidizing agent is used,  $\text{Cl}^-$  may be identified, if  $\text{Br}^-$  is known to be absent. Similarly  $\text{KI}$  and starch may be used to identify  $\text{Br}^-$  or  $\text{Cl}^-$ , if only one of these is present. It is also possible to test for  $\text{Br}_2$  and  $I_2$  simultaneously with a single oxidation, by placing a drop of *m*-phenylenediamine hydrochloride solution and one containing starch grains side by side on the slide which covers the crucible.

**Hypohalites** —  $\text{ClO}^-$ ,  $\text{BrO}^-$ ,  $\text{IO}^-$ . — Strictly speaking, these salts belong with those of the acids whose silver salts are soluble in water, but this classification is of little use in analysis, for the instability of the hypohalites is such that they are in effect characterized more by their oxidizing power and by their decomposition products, than by the reactions of the theoretically pure compounds themselves. Hypohalites are present in any solution of a halogen in water, and conversely their solutions decompose readily on acidification to liberate the halogen. Heating a solution of a hypohalite causes it to be transformed to a

mixture of the corresponding halide and halate; thus a hypochlorite will give a precipitate of  $\text{AgCl}$  with  $\text{Ag}^+$ , and a hypoiodite, one of  $\text{AgI}$  and  $\text{AgIO}_3$ . The identification of the decomposition products of the hypohalites is simple. But since these decomposition products alone do not identify the hypohalite, evidence of its oxidizing power is necessary.

Solutions of hypohalites ordinarily smell of the free halogen; even such a weak acid as  $\text{H}_2\text{CO}_3$  decomposes hypochlorites, forming  $\text{HClO}$ , which is unstable and gives off  $\text{Cl}_2$ . Any tests employed for the identification of the free halogens are best carried out in test drops, exposed to the hypohalite contained in a micro crucible.

$\text{Cl}_2$  from decomposition of hypochlorites may be identified by the precipitate of  $\text{AgCl}$  which it gives with a test drop of  $\text{AgNO}_3$ , or by similar reactions with  $\text{Pb}^{++}$  or  $\text{Tl}^+$ . The fact that the chloride is the only substance precipitated (any chlorates formed being soluble) is distinctive, since  $\text{Br}_2$  or  $\text{I}_2$  will give precipitates of bromates or iodates, in addition to the insoluble halide, and these may be recognized by their anisotropic character.

If  $\text{Br}_2$  is known to be absent,  $\text{Cl}_2$  may be recognized by its oxidizing action on  $\text{KBr}$ ; a test drop containing a little  $\text{KBr}$  and some *m*-phenylenediamine hydrochloride is exposed to the gas, and if  $\text{Cl}_2$  is present a test for  $\text{Br}_2$  will be obtained in the drop.

$\text{Br}_2$  from hypobromites is identified by the *m*-phenylenediamine reaction. The fact that insoluble  $\text{AgBrO}_3$  is formed, as well as  $\text{AgBr}$ , is also of value.

$\text{I}_2$  from hypoiodites is recognized by the starch reaction; with  $\text{AgNO}_3$ ,  $\text{AgIO}_3$  and  $\text{AgI}$  are precipitated. The other reactions for  $\text{I}^-$  may be applied, if desired, for confirmatory tests.

**Chlorites** are of rare occurrence, and are notably unstable, particularly in solution, so that they are not as likely to be present in an unknown as are the other halogen acids. Their decomposition to  $\text{Cl}^-$  and  $\text{ClO}_3^-$  is common, while their formation, generally from chlorine dioxide, is very likely to be accompanied by the formation of  $\text{ClO}_3^-$ .

All chlorites are soluble except those of lead and silver. Of these two,  $\text{Pb}(\text{ClO}_2)_2$  is the more useful in analysis, for it may be precipitated in very weakly acid solution and is moderately stable; but if the solution is more than slightly acid this salt is readily soluble, with the evolution of the gas  $\text{ClO}_2$  and the formation of  $\text{Cl}^-$  in solution.  $\text{Pb}(\text{ClO}_2)_2$  forms very fine-grained platelets and tiny prisms and crosses which are highly refractive and strongly birefringent.

$\text{AgClO}_2$  is formed only in alkaline solution and is moderately soluble;

its habit appears to vary considerably with the conditions of precipitation, and it is probable that the composition of the precipitate varies also; but since only anisotropic crystals are obtained, this serves definitely to distinguish  $\text{AgClO}_2$  from  $\text{AgCl}$ .

**Halates** —  $\text{ClO}_3^-$ ,  $\text{BrO}_3^-$ ,  $\text{IO}_3^-$ . — The analytical properties of the halates differ in that all chlorates are soluble while bromates and iodates form numerous insoluble salts. For this reason chlorates will be discussed separately.

**Chlorates**, because they form no insoluble salts, cannot be identified directly by precipitation tests, though this negative character is not without value. Recourse must be had to some indirect procedure, either oxidation or reduction of  $\text{ClO}_3^-$ , and identification of the reaction products.

(1) *As Perchlorates.*

Chlorates may be transformed to perchlorates by heating to dryness with  $\text{H}_2\text{SO}_4$ , but the  $\text{HClO}_4$  formed is volatile, and may be lost. The  $\text{H}_2\text{SO}_4$  is supposed to serve as a preventive of overheating, as well as to facilitate the reaction, but neither function is performed perfectly enough to make the transformation even approximately quantitative. The  $\text{ClO}_4^-$  formed is recognized by the precipitate it gives with K, preferably in the presence of  $\text{MnO}_4^-$ . (See Fig. 42, page 69.) In practice, the above method has many shortcomings, and is not always reliable on a micro scale.

The oxidation of  $\text{ClO}_3^-$  to  $\text{ClO}_4^-$  by persulphates, using  $\text{Ag}^+$  as a catalyst, does not appear to yield results suitable for microanalysis.

(2) *Reduction to Chloride.*

A more reliable method of identifying  $\text{ClO}_3^-$  is by reducing it to  $\text{Cl}^-$ . Hydroxylamine sulphate does not accomplish this, though it does reduce  $\text{BrO}_3^-$  and  $\text{IO}_3^-$ ; but sulphites, ferrous salts, or metallic zinc in acid solution are very effective. The  $\text{Cl}^-$  formed is identified in the usual way, with  $\text{Ag}^+$ ,  $\text{Pb}^{++}$ , etc. The zinc metal should be removed before the salts of the heavy metals are added, or these will be "plated out" and will not be available for the test.  $\text{SO}_2$  is very useful for the reduction of  $\text{ClO}_3^-$  to  $\text{Cl}^-$ , when the introduction of a salt into the solution might be undesirable. It may be generated in a micro crucible, and the drop to be tested exposed to the action of the gas, and then tested for  $\text{Cl}^-$  with  $\text{Ag}^+$ , or the  $\text{Ag}^+$  may be put into the test drop before it is exposed to the  $\text{SO}_2$ . In either case sufficient  $\text{HNO}_3$  must be present to prevent the precipitation of  $\text{Ag}_2\text{SO}_3$ , which might be confused with  $\text{AgCl}$  formed from  $\text{ClO}_3^-$ .

The sensitivity of the reduction test for  $\text{ClO}_3^-$  is about 20  $\mu\text{g.}$  per drop of solution.

Since  $\text{AgBrO}_3$  is slightly soluble, especially in hot water, there is a possibility of  $\text{BrO}_3^-$  appearing in the group with  $\text{ClO}_4^-$  and  $\text{ClO}_3^-$ , though unless a very small amount of  $\text{BrO}_3^-$  is present it will have been identified in the group of acids giving silver salts insoluble in  $\text{HNO}_3$ . If there is any question as to a positive test for  $\text{ClO}_3^-$  (by reduction) being due to  $\text{BrO}_3^-$ , the reduction test using *m*-phenylenediamine hydrochloride (see page 378), may be applied to the solution of  $\text{AgBrO}_3$ , and thus even a small amount of  $\text{BrO}_3^-$  may be detected in the presence of  $\text{ClO}_3^-$ . If a small amount of  $\text{ClO}_3^-$  is present with a large amount of  $\text{BrO}_3^-$ , the identification is less simple. The chromyl chloride test is applicable where no other compounds of chlorine are present. It is also possible to reduce  $\text{BrO}_3^-$  with hydroxylamine sulphate, which will not reduce  $\text{ClO}_3^-$ , precipitate, and filter off the  $\text{AgBr}$ , and test for  $\text{ClO}_3^-$  in the filtrate by reduction with metallic zinc, or  $\text{FeSO}_4$ , etc. This procedure is indirect, and is only moderately satisfactory on a micro scale.

### (3) Formation of $\text{ClO}_2$ .

The reaction of concentrated  $\text{H}_2\text{SO}_4$  with a dry chlorate forms chlorine dioxide as well as  $\text{HClO}_4$ , and the  $\text{ClO}_2$  may be made the basis of a useful test. The deep yellow color of the  $\text{ClO}_2$ , either as a gas or, better, dissolved in the  $\text{H}_2\text{SO}_4$ , is apparent when the dry residue of a drop containing about 30  $\mu\text{g.}$   $\text{ClO}_3^-$  is moistened with a small amount of concentrated  $\text{H}_2\text{SO}_4$ .

$\text{ClO}_2$ , evolved in a micro crucible, may also be recognized by means of a hanging drop test with  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  solution.  $\text{Pb}(\text{ClO}_2)_2$  is formed, as described under the reactions of chlorites.

### A. Group Reactions of Bromates and Iodates.

1.  $\text{AgNO}_3$  gives, with bromates, colorless crosses and short, pointed, tetragonal prisms, appearing almost opaque on account of their high refractive index; they are moderately birefringent and show parallel extinction.  $\text{AgBrO}_3$  is appreciably soluble in water, especially if warmed, and may be recrystallized by cooling. It may also be separated from  $\text{AgIO}_3$  fairly well by extraction. The limit of precipitation is about 40  $\mu\text{g.}$   $\text{BrO}_3^-$  per drop.

With iodates,  $\text{AgNO}_3$  forms a fine granular precipitate, but in the presence of a small amount of  $\text{HNO}_3$  characteristic acicular crystals, single and in radiating and flocculent masses, are obtained. They are highly refractive, with strong birefringence and parallel extinction. The sensitivity of this reaction is about 2  $\mu\text{g.}$   $\text{IO}_3^-$  per drop.

2. Barium salts give an appreciably soluble precipitate with  $\text{BrO}_3^-$

in concentrations greater than about 200  $\mu\text{g.}$  per drop. Highly refractive monoclinic prisms, which show rather weak birefringence and an extinction angle of about  $15^\circ$ , are formed. With  $\text{IO}_3^-$ , similar but less soluble crystals are obtained, as prisms, crosses, rhombs, and rosettes, which grow more perfect on standing (Fig. 66, page 105). The sensitivity is about 20  $\mu\text{g. IO}_3^-$  per drop.

Both  $\text{Ba}(\text{BrO}_3)_2$  and  $\text{Ba}(\text{IO}_3)_2$  tend to supersaturate, and crystallization may need to be encouraged by scratching the slide. The precipitate thus obtained clings to the glass, and may easily be washed by decantation. A confirmatory test with  $\text{AgNO}_3$  may then be carried out, either in the saturated solution of the barium halates, or after dissolving them in a small amount of dilute  $\text{HNO}_3$ . This permits a separation of  $\text{BrO}_3^-$  and  $\text{IO}_3^-$  from the halides or from  $\text{IO}_4^-$ .

3. Lead salts give, with  $\text{BrO}_3^-$ , prisms very similar to those of  $\text{Ba}(\text{BrO}_3)_2$ . With  $\text{IO}_3^-$ , a fine granular precipitate is obtained, which on standing develops into curving and branching forms. Fine needles, radiating and in sheaves, are formed from more dilute solutions.

4.  $\text{TlNO}_3$  yields fourlings and clusters of cubes, moderately birefringent, with  $\text{BrO}_3^-$ ; and similar but less soluble and more branching crystals with  $\text{IO}_3^-$ .

5.  $\text{NH}_4\text{IO}_3$  and  $\text{Ca}(\text{IO}_3)_2$  are insoluble enough to be precipitated from fairly concentrated solutions of iodates, whereas the corresponding bromates are soluble.

#### *B. Reduction of Bromates and Iodates.*

Reduction of  $\text{BrO}_3^-$  to  $\text{Br}_2$ , or  $\text{IO}_3^-$  to  $\text{I}_2$ , is a valuable means of identification, for the liberated halogen can then be recognized just as when obtained by the oxidation of halides. (See page 375.) A great number of reducing agents are suitable, but the best are hydrazine sulphate, hydroxylamine sulphate, phenylhydrazine hydrochloride, or hydroquinone. Nascent hydrogen, from zinc (plus a trace of a copper salt, to form a "couple"), is the most satisfactory of the inorganic reducing agents. In carrying out the reaction it should be borne in mind that an excess of the reagent may carry the reduction so far as to form the halides instead of the free halogen. The solution should be acidified with  $\text{H}_2\text{SO}_4$ ; gentle warming is advantageous.

The reduction of halate to halogen may be carried out in either of two ways:

- (1) In the same drop with the reagent used to test for the free halogen.
- (2) In a micro crucible, with the test reagent in a hanging drop.

In applying the former of these methods to bromates, the organic

reducing agents interfere with the *m*-phenylenediamine test for  $\text{Br}_2$ , so metallic zinc should be used for the reduction. The sensitivity of this method is about 30  $\mu\text{g. BrO}_3^-$  per drop.

If the  $\text{Br}_2$  liberated by reduction is identified in a separate drop, the choice of reducing agent is not restricted, and the method is of more general application. The solution to be tested is placed in a micro crucible, acidified with  $\text{H}_2\text{SO}_4$ , and a fragment of the reducing agent is added. Cautious warming aids in liberating the  $\text{Br}_2$ . The test drop of *m*-phenylenediamine hydrochloride is employed just as in testing for bromides. (See page 378.)

In the case of iodates the choice of a reducing agent is not restricted, and the test with starch is practically as sensitive by either method — about 4  $\mu\text{g. IO}_3^-$  per drop.  $\text{IO}_4^-$  likewise yields  $\text{I}_2$  on reduction, so its absence must be established by independent tests.

$\text{BrO}_3^-$  and  $\text{IO}_3^-$  may be tested for simultaneously, by using two hanging drops of the appropriate reagents.

### Periodates — $\text{IO}_4^-$ .

#### A. With Silver Nitrate.

The physical chemistry of the silver periodates is somewhat in question,<sup>27</sup> and the acidity of the solution has a marked effect upon the nature of the precipitate obtained with  $\text{Ag}^+$ . From neutral or very slightly acid solutions of  $\text{IO}_4^-$  a precipitate is obtained which is satisfactory as a test, even though opinion is divided as to whether it consists of  $\text{Ag}_3\text{IO}_5$  or  $\text{Ag}_5\text{IO}_6$ . It is yellow to orange at first, fine-grained, highly refractive, and probably owes its light color to its fine state of subdivision and high index of refraction. On standing, preferably on heating, the fine particles grow and their crystal form becomes apparent, while the color of the precipitate darkens nearly to black. No phase transformation seems to be involved, for the fine grains first formed, as far as can be observed, have a habit similar to the crystals developing later. These last are hexagonal and triangular plates and stars, which may change into snowflake forms. They are dark brown by transmitted light, or, if finely enough divided, yellow. Birefringence is fairly strong. The precipitate may be dissolved in  $\text{HNO}_3$  and reprecipitated by  $\text{NH}_4\text{OH}$ , but only fine crystalline grains are obtained by this procedure.

If the precipitation takes place in a solution containing an appreciable amount of  $\text{HNO}_3$ , a different type of crystals appears. These have been given the formula  $\text{Ag}_2\text{H}_3\text{IO}_6$  (or  $\text{Ag}_4\text{I}_2\text{O}_9 \cdot 3 \text{H}_2\text{O}$ ). The crystals are pale straw-yellow, acute rhombohedral in habit, exhibiting symmetrical

<sup>27</sup> Mellor: *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. II, p. 410 (1922).

extinction and fairly strong birefringence. They are very soluble in  $\text{HNO}_3$ , and if more than a very small amount of the latter is present they will not be formed.

From solutions strongly acid with  $\text{HNO}_3$ , or from  $\text{HNO}_3$  solutions of either  $\text{Ag}_2\text{H}_3\text{IO}_6$  or  $\text{Ag}_5\text{IO}_6$ , a third type of crystals may be obtained. These are highly soluble, and are unlikely to occur in a test. They are tetragonal bipyramidal in form, and are isomorphous with  $\text{KIO}_4$ , so their formula must be  $\text{AgIO}_4$ . They are yellow in color, more soluble than  $\text{KIO}_4$ , are highly refractive, and show strong birefringence. On the addition of water these crystals decompose to a fine-grained mass, composed of tiny but typical crystals of  $\text{Ag}_2\text{H}_3\text{IO}_6$ .

Of all the above precipitates, only the first is insoluble enough for a qualitative test, and it is suitable only under the proper conditions, namely, when the solution to be tested is neutral or *only very slightly acid*. Under these conditions a precipitate of  $\text{Ag}_5\text{IO}_6$  may be obtained with concentrations corresponding to about 20  $\mu\text{g}$ .  $\text{IO}_4^-$  per drop. If more than a very small amount of acid is present, only very concentrated solutions of periodates are likely to give a precipitate. The color of the freshly precipitated, finely subdivided  $\text{Ag}_5\text{IO}_6$ , and its subsequent development of characteristic crystals, with darkening color, are typical, and serve to identify  $\text{IO}_4^-$ . The only other colored silver precipitate likely to be confused with the  $\text{Ag}_5\text{IO}_6$  is  $\text{Ag}_3\text{AsO}_4$ , but, since this is much less readily soluble in  $\text{HNO}_3$ , forms crystals bristling with long slender needles, and may be identified by other tests,  $\text{AsO}_4^{3-}$  is not likely to lead to error.  $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_2\text{Cr}_2\text{O}_7$  are also colored, but they do not exhibit any sequence of color changes, are of entirely different crystal habit, and, unless so thick as to appear opaque, are of a clearer, much more reddish hue by transmitted light.

B. As confirmatory tests for  $\text{IO}_4^-$  a number of reactions are available.  $\text{K}^+$  gives with  $\text{IO}_4^-$  a characteristic precipitate of  $\text{KIO}_4$ , acute tetragonal bipyramids, of fairly strong birefringence, not readily soluble in  $\text{HNO}_3$ . These are obtained in concentrations greater than about 40  $\mu\text{g}$ .  $\text{IO}_4^-$  per drop.  $\text{Rb}^+$  and  $\text{Cs}^+$  give similar crystals, rather more soluble in water. This precipitation of  $\text{KIO}_4$  is of the same order of sensitivity as that of  $\text{KClO}_4$  as a test for  $\text{ClO}_4^-$ , and is very distinctive, for acids giving potassium salts of such low solubility are few indeed.

### C. Reduction to Iodine.

Periodates are reducible to iodine in much the same manner as are the iodates. (See page 383.) The iodine is identified by the starch reaction. It is possible thus to detect iodates in concentrations corresponding to about 20  $\mu\text{g}$ .  $\text{IO}_4^-$  per drop.

This reduction is also applicable to the  $\text{Ag}_5\text{IO}_6$  precipitate, which is

dissolved in a very slight excess of  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$ , and acted upon by the reducing agent (hydroxylamine sulphate, metallic zinc, etc.). A very fine white precipitate of  $\text{AgI}$  is formed. The reaction with starch does not take place, probably because of the precipitation of all the iodine in the form of very insoluble  $\text{AgI}$ .

*D.* The fact that  $\text{Ba}^{++}$  gives no precipitate with  $\text{IO}_4^-$  aids in differentiation from  $\text{IO}_3^-$ , or in separating  $\text{Ba}(\text{IO}_3)_2$  by precipitation so that the filtrate may be tested for  $\text{IO}_4^-$  with  $\text{Ag}^+$ ; or with  $\text{Bi}(\text{NO}_3)_3$  kept in solution with a very little  $\text{HClO}_4$ .<sup>28</sup>

### Perchlorates — $\text{ClO}_4^-$ .

#### *A. With Potassium.*

The most distinctive reaction of the salts of perchloric acid is the formation of a characteristic precipitate with  $\text{K}^+$ . Orthorhombic prisms and rhomb-shaped forms are obtained in well-crystallized habit (Fig. 42, page 69). These are isomorphous with  $\text{KMnO}_4$ , and are readily colored (solid solution) by the latter if a little is added to the test drop. The test is thus rendered more easily observable. Skeleton forms occur if the concentration of  $\text{ClO}_4^-$  is high. (See also Potassium, page 68.) The limit of sensitivity of the above test is about 0.001 gram  $\text{HClO}_4$  per cc. (50  $\mu\text{g}$ . per drop).

*B.* Strychnine sulphate gives a precipitate of simple rectangular, lath-shaped forms with  $\text{ClO}_4^-$ . These have very weak birefringence, parallel extinction, and tend to grow in parallel clusters, especially if the reagent is added as a solid. These crystals cross each other at right angles, overlying the fragment of strychnine sulphate, and giving an appearance similar to a frayed bit of cloth. The concentration of the reagent is best kept low. The sensitivity of this test is about 10  $\mu\text{g}$ . per drop.

Other microscopical reactions of perchlorates are on record, but they are of questionable specificity.

**Mixtures of Halogen Acids.** — The following outline may serve as a guide to the identification of the anions of the halogen acids, especially in mixtures with each other.

Familiarity with the microscopical appearance of the precipitates formed by  $\text{Ag}^+$  and  $\text{Ba}^{++}$  with the various acids may enable the analyst to go at once to specific confirmatory tests and thus greatly shorten the time required for the analysis.

To a drop of the neutral or only very slightly acid solution to be tested add  $\text{AgNO}_3$  solution in slight excess.

<sup>28</sup> Willard and Thompson: *Jour. Amer. Chem. Soc.* 56, 1827 (1934).



A. *No precipitate is obtained.*There may be present..... $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ 

1. Reduce and test for  $\text{Cl}^-$ .
2. Evaporate solution to dryness, add a drop of concentrated  $\text{H}_2\text{SO}_4$ ; there is evolution of  $\text{ClO}_2^-$  and formation of  $\text{ClO}_4$  on heating ..... $\text{ClO}_3^-$
3. Concentrate solution. Add  $\text{K}^+$  and a very little  $\text{KMnO}_4$ . Characteristic crystals ..... $\text{ClO}_4^-$

B. *A precipitate is obtained.*..... $\text{IO}_4^-$ ,  $\text{Cl}^-$ ,  $\text{BrO}_3^-$ ,  $\text{IO}_3^-$ ,  $\text{ClO}^-$ ,  $\text{BrO}^-$ ,  $\text{IO}^-$ ,  $\text{ClO}_2^-$ 

Note color and crystalline character of precipitate. Filter and wash precipitate. Test filtrate as in A.

1. Extract precipitate with dilute  $\text{HNO}_3$  (1 : 10).
  - (a) The precipitate dissolves..... $\text{IO}_4^-$   
Identify by reduction.
  - (b) The precipitate is insoluble in  $\text{HNO}_3$ ; extract repeatedly with hot water.  
Concentrate extracts and test for..... $\text{BrO}_3^-$   
Confirm by reduction of original material.
2. Extract the precipitate with  $\text{NH}_4\text{OH}$  (1 : 4).
  - (a) The precipitate is soluble. Allow the solution to evaporate at room temperature. Examine for crystals  
 $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{IO}_3^-$   
Confirm  $\text{IO}_3^-$  with reduction test;  $\text{Br}^-$  with oxidation test;  
 $\text{Cl}^-$  with  $\text{Ag}^+$  after removal of  $\text{Br}^-$  and  $\text{I}^-$  by oxidation.
  - (b) A residue remains..... $\text{I}^-$ , ( $\text{Br}^-$ )  
Confirm  $\text{I}^-$  with oxidation.

C. In all cases in which a precipitate has been obtained with  $\text{AgNO}_3$ , test for the presence of..... $\text{ClO}^-$ ,  $\text{BrO}^-$ ,  $\text{IO}^-$ ,  $\text{ClO}_2^-$ 

In the Bunsen-Treadwell classification of acids the customary grouping on the basis of the solubilities of barium salts, while not so directly applicable to the identification of the halogen acids, should nevertheless be utilized in conjunction with the system outlined above.

The solubilities of the barium salts of the halogen acids are as follows:

Readily soluble in water:  $\text{BaCl}_2$ ,  $\text{BaBr}_2$ ,  $\text{BaI}_2$ ,  $\text{Ba}(\text{ClO}_3)_2$ ,  $\text{Ba}(\text{ClO}_4)_2$ ,  $\text{Ba}(\text{IO}_4)_2$ .

Very slightly soluble in water:  $\text{Ba}(\text{BrO}_3)_2$ .

Very slightly soluble in water, but soluble in dilute  $\text{HNO}_3$ :  $\text{Ba}(\text{BrO}_3)_2$ .

Not readily soluble in  $\text{HNO}_3$ :  $\text{Ba}(\text{IO}_3)_2$ .

**Manganates —  $\text{MnO}_4^-$ ;  $\text{MnO}_4^-$ .**— Few manganates or permanganates are known. Pure  $\text{K}_2\text{MnO}_4$  and  $\text{Na}_2\text{MnO}_4$  are water-soluble and stable in solution for a short time only. All other manganates of the common cations are practically insoluble in water or are decomposed by it.

$\text{AgMnO}_4$  is one of the few permanganates of low solubility.

Because of the intense color of most manganates and permanganates and their great tinctorial power in solutions, their presence is not easily overlooked. But a pink color does not necessarily mean that  $\text{MnO}_4^-$  ions are present, nor does an intense green prove the presence of  $\text{MnO}_4^-$ . There must be proof of the presence of manganese. (See page 260.) In this connection the isomorphism of perchlorates and permanganates is especially valuable.

**Permanganates —  $\text{MnO}_4^-$ .**— Specific tests applicable to dilute solutions are not available. The pink color of the solution, discharged by reducing substances, and the identification of manganese are sufficient for the identification of this ion. For comparison with the behavior of the other ions the group reactions are indicated below.

*A. Group Reactions.*

1.  $\text{AgNO}_3$  gives no precipitate in dilute solutions. In very concentrated test drops or as test drops pass to dryness, square and rectangular plates and tablets and irregular angular grains separate around the circumference of the drop. These crystals are so dark colored as to appear black by reflected as well as transmitted light.

2.  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  and  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  give no appreciable reaction. On standing, a reduction of  $\text{MnO}_4^-$  by acetate ion takes place and a brown precipitate is formed.

3.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  yields an instantaneous, dark brown flocculent precipitate, changing in part into very tiny spherical granules.

4.  $\text{Ti}(\text{C}_2\text{H}_3\text{O}_2)_3$  yields black, tiny, irregular drusy grains and three-armed and four-armed crosses.

## ORGANIC ACIDS

It is necessary to include among the inorganic acids a discussion of acetates, oxalates, and tartrates because of the frequency with which salts of these acids are used as reagents in microscopical qualitative analysis.

All normal acetates are water-soluble. The least soluble are those of  $\text{Ag}^+$  and  $\text{Hg}^+$ . The use, therefore, of acetates as reagents does not introduce an anion that may give rise to insoluble compounds nor introduce a strong acid.

Many double acetates are known.

The oxalates of the alkalis are water-soluble, but most other oxalates are insoluble. Many of these insoluble oxalates unite with soluble oxalates to form soluble double oxalates.

Both "normal" and "acid" oxalates are common; some of the latter are very complex.

No general statements are possible with reference to the solubilities of the tartrates, for the variations are so great that relative solubilities cannot be deduced from the position of the cations in the Periodic System.

The tests outlined for the three organic anions are to be regarded by no means as identification tests but merely a presentation of crystallization phenomena which may arise in the course of microscopical inorganic analyses when acetates, oxalates, or tartrates may be present and unsuspected.

#### Acetates — $(C_2H_3O_2)^-$ .

A.  $AgNO_3$  added by Method I to concentrated neutral test drops yields pearly scales of  $AgC_2H_3O_2$  (Fig. 226, page 391). These soon develop into long, thin plates with more or less irregular sides and ends. Many of these plates become six-sided with terminal angles of about  $90^\circ$ , and exhibit parallel extinction (Fig. 227, page 391).

B. To confirm the test, add  $H_3PO_4$  and distil off the  $HC_2H_3O_2$ , absorbing it in a hanging drop containing a trace of  $NH_4OH$  or  $NaOH$ . Test the hanging drop by one of the tests for acetic acid (acetates).

C.  $HgNO_3$ , added by Method I to a concentrated test drop, gives colorless plates and prisms. Six-sided prisms have their terminal angles equal to  $100^\circ$  and exhibit parallel extinction (Fig. 213, page 355). If the concentrations are not favorable a vast number of floating dendrites and irregular crystalline grains are formed. Often these grains exhibit a most curious phenomenon in that they arrange themselves in symmetrical serried rows.

D. The formation of sodium uranyl acetate<sup>29</sup> (see Sodium, page 51) is one of the most characteristic reactions of  $(C_2H_3O_2)^-$ . The best combination is that suggested by Behrens — uranyl formate<sup>30</sup> and sodium formate. The test for acetates with the formate reagents is performed in the same manner as with uranyl nitrate. The specific

<sup>29</sup> Behrens-Kley: *op. cit.*, p. 314.

Kruger and Tschirch: *Mikrochemie* 7, 318 (1929).

<sup>30</sup> Uranyl formate is easily prepared by precipitating uranyl nitrate with  $NH_4OH$ , washing the precipitate, dissolving in formic acid, and evaporating on the water bath to crystallization. Recrystallize if necessary.

reaction is the formation of isotropic tetrahedra of sodium uranyl acetate. Ammonium salts should not be present in excess.

The solution of the unknown material must be approximately neutral and must not contain free alkalis or mineral acids.

**Oxalates** —  $(C_2O_4)^{--}$ . — The appearance of the crystals obtained in testing for oxalates depends upon the nature of the cations present and the concentration of the oxalate ions. Acid, normal, and double oxalates, in stable and metastable forms, abound, according to concentration and temperature conditions.

The statements given below apply to reactions obtainable with oxalates of the alkalis or ammonium. (See page 120.)

*A. Group Reactions.*

1. With  $AgNO_3$  the usual reaction obtained is that of a heavy, white, "amorphous" precipitate soon becoming crystalline, especially in the outer zone. Crystalline grains are formed of very irregular outline, small dendritic masses abound, and here and there areas can be found consisting of irregular disks, and rhomboidal and hexagonal-shaped thin plates. The crystals are always very small and require a magnification of not less than  $200\times$  to reveal their habit (Fig. 231, page 391). On long standing, highly refractive prisms, singly and in radiating clumps, may be formed.

2.  $Ba(C_2H_3O_2)_2$  yields a granular precipitate, changing at once into long, slender, dendritic bunches of very fine needles. These develop into branching aggregates in wisps, crosses, and radiates, the component arms of which may be straight or curved, rough, bristling, or branched. Their appearance is very characteristic and has already been referred to under barium, page 115. In a very short time the entire precipitate becomes converted into these peculiar dendritic aggregates (Fig. 82, page 111).

3. With  $Ca(C_2H_3O_2)_2$  a colorless sandy precipitate is first formed. In the outer zone there soon appear small bristling radiates, X's, and skeleton crystals in thin irregular plates, scales and crosses. All crystals are very thin and never grow large (Fig. 80, page 111).

4.  $Pb(C_2H_3O_2)_2$  yields a dense, white, curdy precipitate becoming sandy. A few small radiates and crosses can be found in certain restricted areas.

5. With  $Tl(C_2H_3O_2)$  no precipitate is obtained and no separation of crystals until the test drop passes to dryness. But in very concentrated test drops rhombs and "prisms" may form.

**Tartrates** —  $(C_4H_4O_6)^{-}$ . — The remarks made relative to the appearance of the crystals in testing for oxalates apply with equal force to the tartrates. The nature of the salt formed, whether an acid or

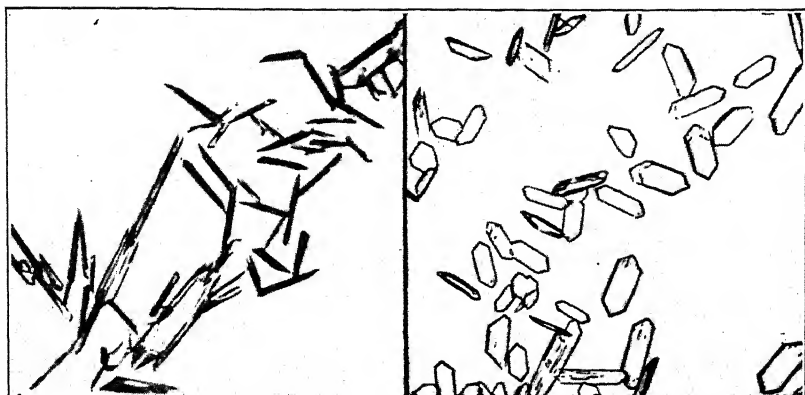


FIG. 226.  $(\text{C}_2\text{H}_3\text{O}_2)^-$  with Silver Nitrate. 100 $\times$ .

FIG. 227.  $(\text{C}_2\text{H}_3\text{O}_2)^-$  with Silver Nitrate. 100 $\times$ .



FIG. 228.  $(\text{C}_4\text{H}_4\text{O}_6)^{--}$  with Silver Nitrate. 100 $\times$ .

FIG. 229.  $(\text{C}_4\text{H}_4\text{O}_6)^{--}$  with Silver Nitrate. 100 $\times$ .

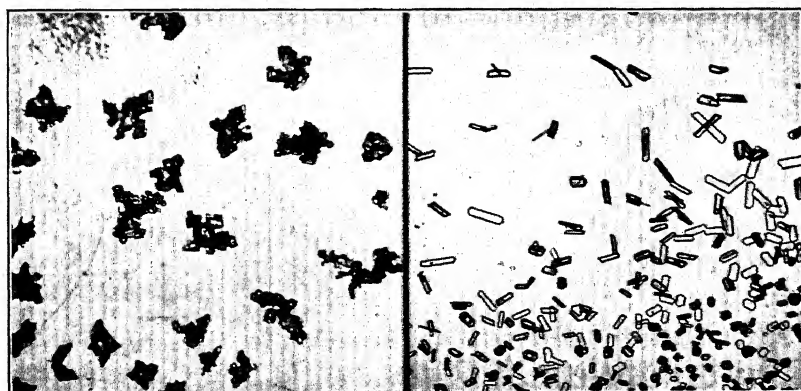


FIG. 230.  $(\text{C}_4\text{H}_4\text{O}_6)^{--}$  with Lead Acetate. 100 $\times$ .

FIG. 231.  $(\text{C}_2\text{O}_4)^{--}$  with Silver Nitrate. 200 $\times$ .

normal tartrate or whether a double tartrate will be obtained, will depend upon concentrations and temperatures.

In order to obtain a separation of tartrates in a test drop, the solution must be practically saturated with respect to  $(C_4H_4O_6)^{--}$ .

*A. Group Reactions.*

1.  $AgNO_3$  produces a flocculent white precipitate, instantly changing into large mossy radiates which appear to be light brown by transmitted light (Figs. 228, 229, page 391). There are also formed on standing stout, very irregular, angular prismatic grains. Short monoclinic prisms and "knee twins" of the bitartrate appear if the test is made in slightly acid solution. These prisms are strongly birefringent and are highly refractive.

2. With  $Ba(C_2H_3O_2)_2$ , no precipitate and no separation of crystals takes place, but on standing a very fine granular precipitate may form at the circumference of the test drop near where the reagent was caused to flow in. It is seldom that distinct crystals can be obtained. Usually when the drop goes to dryness nothing more than a crystalline crust is obtained.

3. With  $Ca(C_2H_3O_2)_2$  the reaction obtained is usually similar in all respects to that given by  $Ba(C_2H_3O_2)_2$ , but if the very concentrated (with respect to  $C_4H_4O_6^{--}$ ) test drop is run into a concentrated solution of a calcium salt there will be obtained after a short time large, well-formed, colorless, highly refractive orthorhombic prisms. Since calcium tartrate is moderately soluble in water, but insoluble in alcohol, the addition of a little alcohol will cause the separation of crystals before the test drop passes to dryness (Fig. 72, page 109).

The presence of magnesium salts interferes with the separation of calcium tartrate.

4.  $Pb(C_2H_3O_2)_2$  yields a heavy, white, curdy precipitate. On standing there are formed in the outer zone very characteristic, large, coarse, thick dendrites composed of prismatic grains (Fig. 230, page 391).

But in highly concentrated test drops or in preparations which have stood for some time, thin prisms and four-sided tablets are obtained exhibiting parallel extinction and strong birefringence.

5. With  $Tl(C_2H_3O_2)$  no precipitate and no separation of crystals occurs unless there is a very high concentration of tartrate ions.

*B.* When a chloride of the potassium group is added to very concentrated solutions of tartrates, a separation of an alkali tartrate may occur, providing the conditions are favorable for the formation of an acid tartrate. (See page 72. Fig. 41, page 61.) If  $CsCl$  is employed it must be borne in mind that any one or more of very many double chlorides may be formed and separate in the test drop.

## CHAPTER XII

### SPECIAL REAGENTS YIELDING REACTIONS WITH A NUMBER OF CATIONS

There are a number of reagents and reactions of doubtful value as identification tests for specific cations or anions which are nevertheless of unquestioned usefulness in a preliminary study of mixtures of unknown composition since they may yield information which may materially shorten the time required for the completion of an analysis.

The most useful of these are hexamethylenetetramine, potassium ethyldithiocarbonate, fibers carrying zinc sulphide, and the precipitation of other metals by metals which are more electropositive.

#### Reactions Obtainable with Hexamethylenetetramine<sup>1</sup>

**Hexamethylenetetramine**—known also as Hexamine; Hexamethyleneamine; Methenamine; Formin; Urotropin.— $C_6H_{12}N_4$  or  $(CH_2)_6N_4$  is a univalent base forming direct addition products with most anions and the salts of most cations.

The free base is readily soluble in cold water, less soluble in hot water, and separates from aqueous solution in well-formed discrete crystals of the isometric system. Its refractive index is approximately 1.59.

Because hexamethylenetetramine forms direct addition compounds, the crystals separating in test drops may contain both the cations and the anions which may be present. A test drop containing two or more salts which differ in both cations and anions may therefore yield results decidedly puzzling, often not interpretable.

With many salts more than one combination is possible, depending upon the ratio of reagent to salt and whether free acid is present or absent. In order to reduce the number of variables it has been found best always to acidify the test drop with HCl 1 : 3 (or, if nitrates must

<sup>1</sup> Vivario and Wagenaar: *Pharm. Weekblad*, **54**, 157 (1917); *Chem. Zentral.* **88**, 224 (1917); *Zeit. anal. Chem.* **58**, 228 (1919); **67**, 298 (1925).

Denigès: *Schweiz. Apoth. Zeit.* **57**, 497 (1919).

Cole: *Philip. Journ. Sci.* **22**, 631 (1923).

Martini: *Addenda a la Microquímica Especial* (Cordoba, 1926); *Mikrochemie* **6**, 28 (1928).

Altpeter, J.: *Das Hexamethylenetetramine und seine Verwendung* (Knapp, Halle, 1931).

be used,  $\text{HNO}_3$  is employed). Under these conditions the crystals that separate will be, almost always, an addition compound of the chloride of the cation present, corresponding to the general formula  $n[(\text{CH}_2)_6 \cdot \text{N}_4 \cdot \text{HCl}] \cdot m\text{M} \cdot x\text{H}_2\text{O}$ , where  $M$  stands for the metal chloride,  $n$  is either 1 or 2, and  $m$  any multiple from 1 to 5. Some of the addition compounds are anhydrous; some may have one or more molecules of water of crystallization.

The test drop must be moderately dilute when the reagent is added. The test drop must be strongly acidified with  $\text{HCl}$  (1 : 3) and thoroughly mixed. A *large* fragment of the reagent is then introduced into the center of the drop and the preparation allowed to stand undisturbed for a few seconds and then critically studied. The preparation is set aside and again carefully scrutinized from time to time until it passes to dryness. These repeated studies are essential because several different addition products may be formed as the concentration of the test drop changes, and it is important to note any variation in crystal habit which may take place.

As the reagent fragment disintegrates it may give rise to well-formed crystals in a zone just around the fragment; as these crystals move out into the test drop they may dissolve and disappear, but may again separate around the circumference of the drop. To avoid errors the analyst should perform a "blank" with the reagent in  $\text{HCl}$ , so as to become familiar with the crystal habit of hexamethylenetetramine hydrochloride, which separates readily from drops strongly acidified with  $\text{HCl}$ . If a metastable solution results, crush a little of the crystalline crust which forms around the circumference of the drop. Four- and six-sided tablets and plates of the hydrochloride are obtained. Those with four sides generally exhibit oblique extinction, those with six sides, parallel extinction.

The addition of  $\text{HCl}$  to the test drop may cause a precipitate before the addition of the hexamethylenetetramine. If so, any one or more of the following may be indicated.

$\text{Ag}^+$ ,  $\text{Hg}^+$ ,  $\text{Pb}^{++}$ ,  $\text{TI}^+(\text{Cu}^+, \text{Au}^+)$ .

$\text{SiO}_2$  from alkaline silicates or siliceous material.

$\text{TiO}_2$ ,  $\text{CbO}_2$ ,  $\text{TaO}_2$ ,  $\text{H}_3\text{BO}_3$ .

$\text{MoO}_3$ , soluble in excess of  $\text{HCl}$ .

$\text{WO}_3$ , from ortho- and para-tungstates, but not from meta-.

$\text{TeO}_2$  from tellurates and tellurites.

$\text{As}_2\text{O}_3$  from arsenites.

$\text{Sb}$  and  $\text{Bi}$  as basic chlorides.



## Reactions with Hexamethylenetetramine

I. *No separation of crystals and no visible reaction because of the high solubility of the addition compounds.*

Chlorides of Li, Na, K, Rb, Cs,  $\text{NH}_4$ , Co, Ni.

Chlorides of Ca, Sr, Ba (but crystals may separate if the test drop is not dilute).

Chlorides of Be, Al, Mg, Ga, Mn, Cr (but crystals separate in concentrated test drops).

Alkali salts of  $-\text{C}_2\text{H}_3\text{O}_2^-$ ;  $\text{C}_2\text{O}_4^-$ ;  $\text{B}_4\text{O}_7^-$ ;  $\text{SO}_4^-$ ;  $\text{SeO}_3^-$ ;  $\text{SeO}_4^-$ ;  $\text{AsO}_4^-$ ;  $\text{AsO}_2^-$ ;  $\text{I}^-$ ;  $\text{Br}^-$ ;  $\text{Cl}^-$ .

II. *Colorless crystals separate.*

$\text{ZnCl}_2$

Wisps, sheaves, and radiates of long slender needles, or radiates of lath-shaped plates. Crystals moderately birefringent with parallel extinction. Zinc can be detected in the presence of cadmium, and *vice versa*.

$\text{CdCl}_2$

Large, fern-like dendrites made up of hexagonal scales. Hexagonal plates and tablets. Or a drusy crystalline crust at the circumference of the drop, made up of plates and scales. Discrete hexagonal plates and tablets are isotropic and exhibit a positive uniaxial interference figure. The  $\text{CdCl}_2$  addition compound is much more soluble than that of zinc, hence does not make its appearance until after the zinc compound has separated.

$\text{MgCl}_2$

In highly concentrated test drops, small, thin, square or rectangular plates with marked twinning. Elongated plates give parallel extinction. Index of refraction very low.

$\text{HgCl}_2$

Stout anisotropic dendrites growing into "trees" extending completely across the field of the microscope. The branches are arranged in characteristic patterns. Clumps of rhombiform plates may also be formed. Crystals are weakly birefringent with colors of the first order. Under certain conditions octahedra may predominate. In very dilute test drops no dendrites are formed.

$\text{InCl}_3$

Isotropic octahedra first appear followed by thin scales and plates growing into irregular clumps or radiates. In a short time the octahedra change into masses of tiny birefringent crystals and large dendrites are formed. Plates mostly rectangular with oblique extinction and brilliant polarization colors.

$\left. \begin{array}{l} \text{BeCl}_2 \\ \text{AlCl}_3 \\ \text{GaCl}_3 \end{array} \right\}$

The reagent fragment sometimes becomes surrounded by a zone of amorphous precipitate. No crystals separate.

$\text{SbCl}_3$

Highly refractive hexagonal plates, prisms, and foliated aggregates. The prisms are strongly birefringent and exhibit parallel extinction. The six-sided plates and tablets are isotropic. In some concentrations, in addition to the preponderating anisotropic crystals, isotropic octahedra may be formed.

- BiCl<sub>3</sub>** A fine granular precipitate is first formed, soon becoming transformed into well-developed octahedra. No birefringent crystals are to be found (distinction from Sb) and no six-sided plates or tablets. By varying the concentrations in several drops it is possible to distinguish between Bi and Sb.
- SnCl<sub>4</sub>** In highly concentrated test drops the reagent fragment becomes covered at once with a crystalline coating which renders it opaque and brown by transmitted light. In more dilute drops dendrites appear as the fragment disintegrates; these dendrites rapidly develop into highly refractive skeleton prisms exhibiting strong birefringence and brilliant colors. Under certain conditions octahedra may be formed, but much smaller than those of Bi.
- HgNO<sub>3</sub>** Test drops strongly acidified with HNO<sub>3</sub> yield, first, tiny, highly refractive acicular crystals, singly and in irregular clumps, X's, and radiates. Later, large, thin plates are formed in foliated masses. These plates are strongly birefringent with oblique extinction of about 14°; polarization colors of 2nd and 3rd orders. If spontaneous evaporation is not too rapid, short, stout prisms having acute ends develop.
- TlNO<sub>3</sub>** Concentrated test drops (with HNO<sub>3</sub>) yield strongly birefringent, elongated, six-sided plates and tablets with terminal angles of 120° and extinction angle of 40°; polarization colors, 2nd and 3rd orders.
- AgNO<sub>3</sub>** In dilute test drops acidulated with HNO<sub>3</sub> there are formed long, slender prisms with very acute or broken ends, long, thin, lath-like plates with parallel extinction, and short, stout, highly refractive bipyramidal prisms, the last in a zone around the fragment. All are strongly birefringent. The crystals disintegrate on standing.
- Pb(NO<sub>3</sub>)<sub>2</sub>** In HNO<sub>3</sub> solutions, after a short interval of time, clumps of large dendrites appear and a crystalline crust is formed at the circumference of the test drop. This crust is coarsely crystalline and is composed of a conglomerate of dendrites, highly refractive, strongly birefringent prisms, elongated plates and tablets; the latter are generally six-sided with an extinction angle of about 16°.
- Metatungstates** Immediate precipitation of tiny, four-sided plates with incurving sides. There is usually a marked rhythmic formation of rings made up of tiny angular grains. These grains may develop into dendrites, needles, and plates. Ortho- and para-tungstates are decomposed by HCl.
- Molybdates** Test drops in which MoO<sub>3</sub> was precipitated by the addition of the HCl and was subsequently dissolved yield an amorphous precipitate, slowly becoming granular.

Near the reagent fragment clumps of very tiny needles, dendrites, or irregular radiates are formed.

III. *Yellow crystals separate.*

$\text{AuCl}_3$  ( $\text{HAuCl}_4$ )      Radiates of yellow slender needles. Later strongly pleochroic (yellow to orange-brown) tablets develop. Still later these tablets become covered with a coating of very tiny reddish needles. The tablets are strongly birefringent and exhibit parallel extinction.

$\text{H}_2\text{PtCl}_6$       There is an immediate precipitation of tiny isotropic octahedra and skeletons of octahedra  $(\text{NH}_4)_2\text{PtCl}_6$ ?. In a few seconds curious curving dendrites appear in more or less radiating clusters; these are followed by thin imperfect rhombs, squares, and rectangles, singly and in aggregates. If iridium is present, the crystals are red.

$\text{FeCl}_3$       The reagent fragment becomes covered with a brown film. Later highly refractive, yellow tablets, clumps of thin plates, curious polysynthetic twins, and irregular radiates are formed. The plates and tablets give a uniaxial, negative, interference figure. Test drops must be concentrated.

$\text{V}_2\text{O}_5$  in  $\text{HCl}$       A greenish-yellow amorphous precipitate is formed, but no crystals.

$\text{Fe}(\text{CN})_6$ —      In dilute solutions no visible reaction. In moderately concentrated test drops weakly birefringent, six-sided and rhomboidal plates and tablets separate. On standing, highly refractive, anisotropic, yellow pseudo-octahedra appear.

IV. *Red or brown crystals separate.*

$\text{IrCl}_4$       There is an immediate formation of a brownish-red granular precipitate changing into small crosses, dagger-shaped or three-armed skeleton crystals. Many-faced crystalline grains and tiny octahedra are also present. All crystals appear to be isotropic.

$\text{PdCl}_4$       A buff-colored granular precipitate is first formed, soon changing into radiating mossy aggregates which are almost colorless by transmitted light. Later faintly brown, thin rhombs appear, singly and in foliated clusters. Birefringence weak.

$\text{RhCl}_3$       A light brown amorphous precipitate first appears, followed by the formation of angular crystalline grains which in form closely resemble those obtained with iridium, but are brown not red.

$\text{RuCl}_3$       Tiny dark stars and irregular angular grains are formed in a yellow solution. The color of the solution soon changes to a bluish or plum color not easily discerned by transmitted light but apparent over a white background, especially when the preparation has passed almost to dryness.

**Selenium Compounds** Most selenium compounds are reduced and a red precipitate of selenium is formed.

**NOTE.** When hexamethylenetetramine is used as a qualitative reagent it should be borne in mind that with high concentrations the crystals which separate may be those of the reagent itself. Preparations should be studied before they pass to dryness. The statements made in the above tabulation do not take into account the separation of addition products as the preparations pass to dryness unless it is so stated.

### Reactions Obtainable with Potassium Ethyldithiocarbonate (Potassium Xanthate) $\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{CS}\cdot\text{SK}^2$

At the center of a moderately concentrated test drop of a "neutral" solution of the chlorides of the cations add a large mass of the fine felted needles of potassium xanthate. Observe the appearance of the preparation at once over a white and also over a black background. Then examine the preparation under the microscope. Allow the preparation to stand a few minutes and again examine it under the microscope.

By "neutral" solution is here meant the solution of the normal salt without any excess of free acid. Free acids, and even the "acidity" of certain salts, decompose the reagent with the formation of what appears to be a white precipitate but which under the microscope is seen to consist of tiny globules of a colorless oily liquid.

Since a considerable portion of the reagent is likely to be decomposed, it is essential that a much larger amount of the reagent be used than is usual in microscopical reactions. When the oily droplets are so finely dispersed as not to be resolvable by a magnification of  $200\times$ , the reaction product appears to be an amorphous white precipitate and has been so recorded in the tabulation given below. With the chlorides of certain cations the emulsion persists, apparently, independent of such concentrations as are practicable in analysis; with others the dispersed droplets unite, forming oily drops of considerable size, and these in turn may unite to form large patches floating about or more often moving to the circumference of the test drop.

I. *White (colorless) precipitate, or colorless oily drops due to decomposition of reagent. No crystals formed.*

$\text{Be}^{++}$	Oily drops, reagent decomposed.
$\text{Zn}^{++}$	Heavy "amorphous" precipitate.
$\text{Al}^{+++}$	Very fine "amorphous" precipitate, agglutinates on standing.
$\text{Hg}^+$	(Solution of $\text{HgNO}_3$ .) White "amorphous" precipitate, sometimes with yellow patches.
$\text{Ti}^+$	(Solution of $\text{TiNO}_3$ or $\text{Ti}_2\text{SO}_4$ .) Dense gelatinous or curdy mass.

<sup>2</sup> Kotten: *Chemist-Analyst*, No. 48, Nov.-Dec., 1926, has suggested this reagent for macroscopic qualitative analysis.

II. *White (colorless) precipitate. Crystals formed.*

- $\text{Cd}^{++}$  Heavy, white, "amorphous" precipitate, becoming granular. On standing, disk-like radiates of short, very fine needles, and in outer zone dendritic radiates, as evaporation takes place.
- $\text{Pb}^{++}$  Oily drops in outer zone; inner zone, bundles, wisps, and radiates of fine needles.
- $\text{Sb}^{+++}$  (Solution containing free  $\text{HCl}$ .) Oily drops in outer zone; inner zone large colorless or slightly yellow prisms and plates.

 III. *Yellow precipitate, or yellow oily drops. No crystals.*

- $\text{Sn}^{++}$  Bright yellow oily drops; resembles  $\text{Bi}^{+++}$  reaction, but differs in that oily material does not crystallize
- $\text{Sn}^{++++}$  Behaves like  $\text{Sn}^{++}$ .
- $\text{Cu}^{++}$  Bright yellow "amorphous" precipitate, changing slowly to orange.
- $\text{Ag}^{+}$  Bright yellow "amorphous" precipitate, changing to brown and finally to black.
- $(\text{PtCl}_6)^{-}$  Bright yellow "amorphous" precipitate. (Crystals of  $\text{K}_2\text{PtCl}_6$  separate.)
- $\text{OsO}_4$  Faint yellowish-white opalescence, usually invisible under microscope; visible against black background. On standing, agglutinates into "amorphous" masses.
- $\text{Fe}(\text{CN})_6^{4-};$   
 $\text{Fe}(\text{CN})_6^{3-}$  } Brownish-yellow "amorphous" precipitate. See IX.
- $\text{Cr}_2\text{O}_7^{2-}$  Light yellow "amorphous" precipitate, changing into brown.

 IV. *Bright yellow precipitate or yellow oily drops. Crystals are formed.*

- $\text{Bi}^{+++}$  Bright yellow oily drops in which crystallization takes place in a few minutes, with the formation of strongly birefringent, very fine needles in irregular radiates.
- $\text{Tl}^{+++}$  If insufficient reagent is added, the bright yellow "amorphous" precipitate first formed slowly fades to white, and colorless anisotropic hexagonal plates and masses or radiates of fine colorless needles appear. More reagent regenerates the yellow salt; yellow oily drops are formed, and bright yellow, moderately birefringent, irregular, angular grains or masses of very fine dendritic needles or lichen-like radiates. All types may appear in a single preparation. In general, the character of the yellow precipitates varies with the concentration of  $\text{Tl}^{+++}$  and of the reagent.

 V. *Brown precipitate. No crystals.*

- $\text{Fe}^{++}$  Brown "amorphous" precipitate, becoming black.
- $\text{Ni}^{++}$  "Amorphous" brown precipitate.

Pd+++	Brown or buff "amorphous" precipitate in outer zone; on standing becomes granular. Inner zone "amorphous" precipitate mixed with yellow viscous oily drops; on standing these solidify and between crossed nicols are seen to be crystalline, but crystals do not grow to a size to be distinguishable by non-polarized light.
Rh+++	Reddish-brown "amorphous" precipitate.
Au+++	Reddish-brown "amorphous" precipitate. Not same hue as given by Rh.
Cr+++	Faint brownish opalescence.

VI. *Brown precipitate. Crystals formed.*

Fe+++	Very dark brown (or even black) "amorphous" precipitate, and brown or black oily drops. On standing these drops unite, forming yellow-brown or black (by transmitted light) oily patches in which thin, lath-shaped, yellow-brown pleochroic crystals appear.
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VII. *Black precipitate. No crystals.*

Fe++	(See under V.)
Hg+	(Solutions of $\text{HgNO}_3$ .) Black "amorphous" precipitate, and black oily drops.
Co++	Black "amorphous" precipitate.
V+++	Black glutinous "amorphous" precipitate and black oily drops. The precipitate is in reality dark green (?) but is so opaque and dark colored as to appear to be black. The oily drops solidify to a crystalline solid but its habit <i>cannot</i> be discerned under the ordinary conditions of testing.
V+++++	

VIII. *No precipitate is produced, but on standing crystals separate.*

Mn++	Large yellow monoclinic (?) prisms and tablets, strongly birefringent, or thin, lath-shaped, yellow crystals around the circumference of the test drop.
$\text{VO}_3^-$	Colorless or faintly yellow, foliated, prism-like aggregates, often growing to a considerable size.

IX. *No visible reaction.*

$\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Rb}^+$ , $\text{Cs}^+$ , $\text{NH}_4^+$ .	
$\text{Ca}^{++}$ , $\text{Sr}^{++}$ , $\text{Ba}^{++}$ , $\text{Mg}^{++}$ .	
$\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ .	
$(\text{MoO}_4^-)?$ , $\text{CrO}_4^-$ , $(\text{Fe}(\text{CN})_6)^{4-}$ .	Sometimes brownish-yellow precipitate if concentration high.

X. *Deep blue precipitate.*

Ru+++	Dark blue, heavy, granular precipitate. As test drop goes to dryness, color changes to brownish black.
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### Separations of Metals Based upon Differences in Electrical Potentials

Cs<sup>+</sup>  
Rb  
K  
Na  
Li  
Ba  
Sr  
Ca  
Mg  
Al  
Cr  
Mn  
Zn  
Cd  
Fe  
Ti  
Co  
Ni  
Sn  
Pb  
H  
Sb  
Bi  
As  
Cu  
Hg  
Ag  
Pd  
Pt  
Au  
Ir  
Rh  
Os  
Si  
C  
B  
N  
Se  
P  
S  
I  
Br  
Cl  
F<sup>-</sup>

The elements can be arranged in a series such as that shown at the right of this page. Those at the top of the series are strongly electropositive (less "noble"); those at the bottom strongly electronegative (more "noble"). The transition from plus to minus occurs, in the series as given, at cobalt.

The point at which the change of sign from plus to minus occurs depends upon the basis of classification used and the system employed for the calculation of the numerical values of the electropotentials of the different members of the series.<sup>3</sup> In most tables which have been published the change in sign from plus to minus takes place at H, and Co, Ni, Sn, and Pb are considered as electropositive.

The elements above hydrogen in the series can liberate hydrogen from an acid, but those falling below H, *i.e.*, which are more electronegative than H, do not normally give this reaction.

Theoretically any element in the series should be able to precipitate or replace, in an acid solution, any other element lower in the series (less electropositive). As applied in practice there are certain limiting factors which modify the character of the reaction;<sup>4</sup> chief among these are the nature of the metal used, the character of the solution (concentration, acidity, anions present), the temperature, etc.

In making use of this principle in inorganic qualitative analysis,<sup>5</sup> a small, clean, bright fragment of the "reagent" metal is dropped into the somewhat concentrated test drop which has been acidified with HCl. The metal fragment should be small—not over 2 or 3 mm. long by about  $\frac{1}{2}$  mm. wide and thick. It should be handled with forceps so as to avoid a coating of grease from the fingers, and must be completely "wetted" by the solution.

To obtain the best results and the formation of characteristic "trees,"

<sup>3</sup> For these numerical expressions of the electropotentials of the different members of the series, the reader is referred to any one of the more comprehensive textbooks on physical chemistry.

<sup>4</sup> Mellor: *Inorgan. and Theoret. Chem.*, I, p. 1014.

<sup>5</sup> Ward: *Analyst* 58, 28 (1933), has employed this principle in the detection of metal particles in dust, etc. The preparation is treated with a solution of silver nitrate; silver trees were obtained with Cu, Hg, Bi, Pb, Zn, Al, Mg, but not with Sn or Fe.

Staples: *Amer. Mineralogist* 21, 627 (1936), uses a fragment of Zn or Fe for the separation and identification of copper.

the test drop must be just barely acid, the reaction must be slow, and the preparation must rest upon the microscope stage undisturbed.

Since a metal is precipitated upon the reagent in metallic crystals, the precipitate is opaque and all that can be seen by transmitted light is a



Fig. 232. Silver Precipitated by Metallic Zinc. 50 $\times$ .

Fig. 233. Tin Precipitated by Metallic Zinc. 50 $\times$ .

black silhouette. To note the color, hue, and luster, and the full beauty of the crystals, the preparation should always be examined by reflected as well as by transmitted light.

The deposited metal may crystallize either in (1) long, loose dendrites more or less arborescent in character and usually with straight, loose branches at right or acute angles to the main stem (Fig. 233), or the aggregates will resemble a fern frond or a branch of coral; or (2) the crystals may take the form of delicate, more or less curving, feathery or mossy aggregates (Fig. 232); or (3) the "tree" may resemble the second type but the coating upon the reagent-metal is denser, less feathery, and the dendrites will be much shorter and coarser; or (4) the precipitated element may not form a "tree" but will merely plate or coat the reagent or may merely stain it.

Most of the metals depositing in compact, short, mossy trees can also yield trees of the loose feathery or fern-like type. Hence both the compact and loosely branched type may sometimes be obtained from the same test drop.

Elements that merely stain the zinc often fail to yield any perceptible reaction. The stain is readily overlooked as it forms only slowly and may be too thin to be discernible. Usually no stain is obtained until the free acid has combined with the zinc and the active production of hydrogen has ceased and the test drop has passed almost to dryness.



The introduction of metallic zinc into a test drop may sometimes lead to hydrolysis and the precipitation of a non-crystalline basic salt or a hydrous oxide.

The following tabulation of the phenomena produced when a fragment of metallic zinc is introduced into a weakly acidified test drop is offered as a guide which may prove useful in the analysis of materials of unknown composition.

If a precipitate is formed when the test drop is acidified with HCl (see page 394), use a  $\text{HNO}_3$  solution containing only a bare trace of free acid, or decant, filter, or centrifuge from the precipitate and test the clear solution with zinc. The precipitate is washed and analyzed separately.

"Trees" or stains upon the zinc should not be regarded as identification tests, but merely as a guide toward the better planning of a more logical method of attack than might otherwise be adopted.

The electromotive series may also be utilized as a guide to separation of certain metals, in eliminating interferences in analytical testing, or in concentrating or collecting a metal for identification. For example, copper may be removed by placing a drop of the solution on a sheet of zinc or iron, and decanting repeatedly until the metal is no longer blackened by the deposit. The use of copper as a means of concentrating mercury is discussed on page 154.

In any of the above applications it should be remembered that, as one metal ion is discharged, the more electronegative metal passes into solution.

I. *The "tree" is large and loosely branched.*

The branches are simple and are usually straight, meeting the main rib at right or acute angles, and are rarely curved. Trees silvery with pronounced metallic luster.

Ag, Pb, Sn, Tl, In  
(Sb, Bi)

II. *The "tree" is short, compact, mossy, but there may appear after long standing loose-textured, slender, many-branched dendrites.*

The short, compact, mossy type is usually black; the slender many-branched dendrites usually have a metallic luster and the color of the element deposited.

Sb; Bi; Cu; Te; Au; Pd

III. *The zinc is stained brown or black. No "tree" is formed.*

Mn; Ni (Co gives no stain); Rh; Pt; Ir; V; U; Te; Se(red); (Sb); (Bi if Sn present)

IV. *Silvery white globules are formed.*

Hg. The globules are opaque, black by transmitted light, and are distinguishable from bubbles of  $\text{H}_2$  in that they have no bright center.

V. *The zinc remains unaffected but the solution becomes colored.*

Blue — Mo; Ru.

Brown — Ni; Ti.

Red — Ti.

White ppt. — W.

VI. As, Sb yield  $\text{AsH}_3$ ,  $\text{SbH}_3$ .

### Reactions Obtainable with Textile Fibers Impregnated with Sulphides<sup>6</sup>

Guncotton or wool fibers impregnated with zinc sulphide afford a ready and sensitive means of grouping the heavy metals in the same manner as is accomplished when using  $\text{H}_2\text{S}$  and  $(\text{NH}_4)_2\text{S}$  in ordinary qualitative analysis.

The concentrated test drop is acidulated with  $\text{HCl}$  and into it a long "sulphide-fiber" is introduced and thoroughly immersed. Warm very gently and examine at once.

If the fiber does not become colored, allow the preparation to evaporate to dryness, spontaneously. Apply a drop of  $\text{NH}_4\text{OH}$  (1:3), examine under the microscope, and add one or more fresh "sulphide fibers."

*In HCl solution the fiber turns*

Lemon-yellow ..... As, Cd.

Straw-yellow ..... Sn.

Reddish-yellow ..... Sb, Bi.

Brownish-yellow ..... Ag, Sb, Bi, Cu, Hg, Pb, Pt,  
(Mn, Fe, Co, Ni).

Black ..... Ag, Bi, Cu, Hg, Pb, Pt.

*In HCl solutions no change in color, but on adding  $\text{NH}_4\text{OH}$  the fiber turns*

Brown or black. .... Ag, Pb, Hg, Au.

The zinc sulphide fibers should always be tested with known solutions before employing them in the examination of materials of unknown compositions, since the fibers do not always retain their original sensitivity when kept for long periods.

Free  $\text{HNO}_3$  must be absent. To avoid the possible oxidation of  $\text{ZnS}$  to  $\text{ZnSO}_4$  it is a wise precaution always to evaporate to dryness with  $\text{HCl}$ .

The reactions of properly prepared zinc sulphide fibers are very sensi-

<sup>6</sup> Emich and Donau: *Ann.*, 351, 432 (1907).

Chamot and Cole: *Jour. Ind. Eng. Chem.* 9, 52 (1918).

tive in HCl solutions, but far less so and rather unsatisfactory in  $\text{NH}_4\text{OH}$  solutions.

Colors and hues vary with the relative concentrations of the cations present in the test drop and with that of the ZnS in the fiber.

The value of the method lies in the rapidity with which an indication is obtained of the presence or absence of metals yielding colored sulphides.

## CHAPTER XIII

### QUALITATIVE ANALYSIS OF MATERIAL OF UNKNOWN COMPOSITION

A qualitative analysis is usually undertaken for one of the following reasons:

1. To establish fully the chemical constitution of the material under examination.
2. To establish the presence or absence of certain elements or radicals.
3. To test for the presence and nature of impurities.

Microscopical qualitative analyses in themselves yield only chemical information, and if they are to have maximum usefulness must be combined with observations of physical properties, in order that the identity of the actual phases present, and not merely the ions existing in solution, may be established. Furthermore, microscopical analytical methods are particularly appropriate in connection with studies in which the problem of sampling is difficult, and where the individual constituents of the specimen would otherwise have to be treated together instead of being capable of preliminary separation.

**Sampling** for microscopical analyses is likely to present different problems from macroscopical analytical work. If any non-uniformity of composition exists, the aim of microscopical studies should be to detect it, and to ascertain the nature and extent of the local variations, rather than to insure an "average" sample, in which such significant inhomogeneities are too often completely masked.

Ordinarily, therefore, the sampling of any heterogeneous specimen involves a separation of its different constituents, and subsequent testing of some or all of these according to the procedure outlined on subsequent pages. Frequently the minute amount of sample required is the chief justification for the microscopical methods; in any case, sampling or separation is greatly simplified by the fact that a small specimen is sufficient and that only a small quantity of each of its components need be isolated for chemical analysis.

Separation of powdered mixtures into their various ingredients should be accomplished whenever possible, for a reaction may take place between components when brought into solution, although the mixture

may not interact when dry. Even if only one constituent can be separated pure, it should be identified in order that the remaining ones may be ascertained in the dissolved mixture "by difference."

Mixtures in which the different solid constituents are recognizable can usually be separated sufficiently for chemical tests, by rather simple means. (See *Vol. I*, pages 139–148.) Hand sorting, under a magnifier or a Greenough binocular microscope, will be adequate for all but very finely divided material; finely pointed forceps, a glass rod drawn to a point, platinum wire sealed to a piece of glass tube, or capillary pipettes will be found useful for picking up small grains. The rod or wire may be moistened by breathing on them, or rendered slightly sticky by a trace of oil, balsam, vaseline, or glycerine. A miniature spatula, hammered from heavy platinum wire, is convenient for handling particles of all sizes or for scraping up loose material. Dental chisels, needles, or diamond or "Carborundum" splints may be necessary for isolating particles from aggregates of hard materials, such as refractories, ceramic products, minerals, and alloys. Preliminary crushing in a "diamond," or mineralogist's mortar, is often the simplest means of preparing hard and brittle specimens for hand sorting under the microscope.

Dissecting needles, preferably with spear or knife points, will serve for cutting out bits from specimens of soft material, scraping away the outer portion to expose the interior, or removing layers of protective coatings or adhesives.

When circumstances limit the quantity of material handled to a single speck, or when the specimen must not be appreciably damaged by the removal of the sample, special technique is necessary. "Chemical micrurgy,"<sup>1</sup> by means of the micromanipulator (see *Vol. I*, page 144) permits exceedingly minute particles to be handled, or microscopic drops of reagent to be applied for testing *in situ*.

"Streaks" of alloys or minerals,<sup>2</sup> obtained by rubbing on a ground glass or silica plate, furnish material in finely powdered form, with minimum injury to the object studied.

A hypodermic needle, cut off squarely and sharpened, may be used like a "cork borer" to remove tiny "cores," as samples of paintings and other antiquities.<sup>3</sup>

<sup>1</sup> Titus and Gray: *Ind. Eng. Chem. (Anal. Ed.)* 2, 368–71 (1930).

<sup>2</sup> The use of streaks as samples for microchemical testing is discussed by Gaubert: *Comptes rendus* 177, 960 (1923).

See also Strebinger and Holzer: *Mikrochemie* 8, 264 (1930).

<sup>3</sup> Laurie: *Pigments and Mediums of the Old Masters* (1914), p. 19; *The Analyst* 55, 162 (1930).

Gettens: A Microsectioner for Paint Films, *Technical Studies* 1, 20 (1932).

Sifting or winnowing, heavy liquid flotation, or sedimentation in water or other liquid may afford a means of separating powdered mixtures, without the labor of hand sorting.

If the ingredients of a heterogeneous mixture are not readily separable, nor easily soluble, the possibility of testing *in situ* should be borne in mind. The action of the reagent on the individual portions of the sample can be observed under the microscope, and even a single test may afford some clue to the interpretation of analyses made on the mixture as a whole.

Suspended matter in liquids may be collected by sedimentation or by means of the centrifuge. If filter paper fibers are not objectionable, filtration according to the methods given on page 14 may be satisfactory for dealing with small amounts of suspension.

The study of the individual substances obtained for analysis should include physical and chemical observations.

Physical examination should cover the form, size, and distribution of the material. It may well be carried out in connection with sampling operations. The apparent purity of the specimen, or the presence of effloresced, deliquesced, or otherwise altered portions, will often be of significance. It should be remembered that physical examinations rarely use up much of the sample, and that any information which they yield is *in addition* to the chemical evidence.

Physicochemical behavior indicating hydrates, double salts, or the presence of polymorphic substances is often highly significant (see *Vol. I*, pages 351-357) and should be studied as fully as possible, especially in those cases where the nature of a solid phase, rather than the presence of ions in solution, is to be determined. Many double salts, stable under controlled conditions or when dry, cannot be dissolved and recrystallized without decomposition.

A crystallographic examination should always be carried out. (See *Vol. I*, page 311). Its completeness will naturally vary, depending upon whether the material is, or can be prepared, in suitable condition to allow the detailed determination of crystal form and optical properties, and also upon the needs of the analyst.

Ideally, the results of microscopical analytical tests should be used in conjunction with optical descriptions, but adequate crystallographic and optical data have not been tabulated for a large proportion of even the commoner inorganic compounds. It is therefore infrequently the case that the identification can be made primarily on crystal properties, with chemical reactions as confirmatory tests; instead, the analyst will usually have to consider what possible compounds could be present, as represented by the ions found, and then decide between these possi-

bilities on the basis of the observed crystalline character. Mere knowledge of the crystal systems of compounds is rarely useful for such purposes; several different solid compounds of the same ions may exist in a single system, and, furthermore, in many cases the true system may not be determinable with certainty. Such ambiguities are complicated by the necessity of considering hydrates and double salts.

On the other hand, if emphasis is placed not upon crystal system as the criterion for identification, but upon several geometrical and optical properties and constants of the crystals, the findings may be highly conclusive as regards the actual solid phase present. Publications giving crystal descriptions may be helpful in those instances where the substances have previously been studied; but in any case comparison with known samples, crystallized under comparable conditions, is strongly advised as a check upon the tentative interpretation of ionic reactions. Comparison with known samples, crystallized under similar conditions, may speed the course of the analysis greatly, when the possibilities are limited in number. Where reasonably full descriptions and numerical determinations of refractive indices are possible, recourse to published tables of properties may be sufficient for identification,<sup>4</sup> or may greatly limit the required chemical tests.

When the material in hand is distinctly crystalline and isotropic, the authors believe that its identification can be more rapidly accomplished by first testing for the anions.

The number of inorganic salts which are isotropic (cubic system) is relatively small in comparison with the large number which are anisotropic. Often a determination of refractive index and reference to a table<sup>5</sup> will afford an immediate clue as to the probable compound under investigation.

Having identified the anions present, a plan for the search for the cations can readily be made by consulting the following table, which includes most of the isotropic inorganic salts.<sup>6</sup>

<sup>4</sup> Winchell: *Microscopic Characters of Artificial Minerals*. See also the other works cited in Vol. I, pages 320, 321, 323, 324.

<sup>5</sup> Such as that of Winchell: *op. cit.*, p. 162.

<sup>6</sup> Salts of the "rare earths" are not included in the tabulation.

## ISOTROPIC INORGANIC SALTS

*The Material may contain one or more of  
the cations listed below.*

*Anion found:*

Arsenate	Na <sup>+</sup> (as Na <sub>7</sub> F(AsO <sub>4</sub> ) <sub>2</sub> ·19 H <sub>2</sub> O)
Borate	Na <sup>+</sup>
Bromate	Na <sup>+</sup> ; NH <sub>4</sub> <sup>+</sup> ; Mg <sup>++</sup> ; Zn <sup>++</sup> ; Cd <sup>++</sup> (?)
Bromide	Li <sup>+</sup> ; Na <sup>+</sup> ; K <sup>+</sup> ; Rb <sup>+</sup> ; Cs <sup>+</sup> ; NH <sub>4</sub> <sup>+</sup> ; Tl <sup>+</sup> ; Cu <sup>+</sup> ; Ag <sup>+</sup> ; (Si; Ge); Fe <sup>++</sup>
Carbonate	Na <sup>+</sup> Mg <sup>++</sup> , [as Na <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> ·MgCl]
Chloride	Li <sup>+</sup> ; Na <sup>+</sup> ; K <sup>+</sup> ; Rb <sup>+</sup> ; Cs <sup>+</sup> ; NH <sub>4</sub> <sup>+</sup> ; Tl <sup>+</sup> ; Cu <sup>+</sup> ; Ag <sup>+</sup> ; Zn <sup>++</sup> ; Sr <sup>++</sup> ; Sn <sup>++++</sup> ; W <sup>+++++</sup> ; (Pd; Ir; Pt; in complex ions with alkalis)
Chlorate	Na <sup>+</sup>
Cyanide	Na <sup>+</sup> ; K <sup>+</sup> ; Zn <sup>++</sup>
Fluoride	Li <sup>+</sup> ; Na <sup>+</sup> ; K <sup>+</sup> ; Rb <sup>+</sup> ; Cs <sup>+</sup> ; NH <sub>4</sub> <sup>+</sup> ; Ca <sup>++</sup> ; Sr <sup>++</sup> ; Ba <sup>++</sup> ; Pb <sup>++</sup> ; Fluoro-silicates, -zirconates, -titanates of alkalis. Basic aluminum fluoride.
Iodate	Al <sup>+++</sup>
Iodide	Li <sup>+</sup> ; Na <sup>+</sup> ; K <sup>+</sup> ; Rb <sup>+</sup> ; Cs <sup>+</sup> ; NH <sub>4</sub> <sup>+</sup> ; Cu <sup>+</sup> (?)
Nitrate	Ca <sup>++</sup> ; Sr <sup>++</sup> ; Ba <sup>++</sup> ; Pb <sup>++</sup>
Nitrite	Double or Triple Nitrites of Na; K; Rb; Cs; Tl <sup>+</sup> ; NH <sub>4</sub> with Pb; Co; Ni; Cu <sup>++</sup> , Hg <sup>+</sup> , Sr, Ba
Oxide	Cu <sub>2</sub> O, MgO, CaO, SrO, BaO, NiO, CoO, B <sub>2</sub> O <sub>3</sub> , As <sub>2</sub> O <sub>3</sub> . SiO <sub>2</sub> when fused
Phosphate	NaF·2 Na <sub>3</sub> PO <sub>4</sub> ·19 H <sub>2</sub> O; Ag <sub>3</sub> PO <sub>4</sub>
Pyrophosphate	Si, Ti, Sn, Zr
Selenate	Selenate "alums"; only a few are known. Cs <sup>+</sup> , K <sup>+</sup> , Al <sup>+++</sup> , Fe <sup>+++</sup>
Sulphate	Na <sup>+</sup> ; K <sup>+</sup> ; Rb <sup>+</sup> ; Cs <sup>+</sup> ; Tl <sup>+</sup> ; Ag <sup>+</sup> ; NH <sub>4</sub> <sup>+</sup> ; Al <sup>+++</sup> , Cr <sup>+++</sup> , Fe <sup>+++</sup> , Mn <sup>+++</sup> , In <sup>+++</sup> , Ga <sup>+++</sup> , Tl <sup>+++</sup> , Rh <sup>+++</sup> , Ti <sup>+++</sup> , V <sup>+++</sup> in "alums"; Mg <sup>++</sup>
Vanadate	Na <sup>+</sup> ; Alkali fluovanadates
Silicate	Li <sup>+</sup> ; Na <sup>+</sup> ; K <sup>+</sup> ; Al <sup>+++</sup> ; Cu <sup>++</sup> ; Ba <sup>++</sup> ; Mg <sup>++</sup> ; Zn <sup>++</sup> ; Fe <sup>+++</sup> ; Silica gel

**Chemical Examination.**—The application of microscopical qualitative analytical tests to the identification of unknown material is likely to be of limited value if these tests are merely employed empirically, or as a part of some fixed analytical scheme. The reagents serve for so many different tests, and the possible appearances with each are so numerous, that the analyst must keep in mind all the various reactions which may occur, and must be alert to interpret the unexpected phenomena as well as the normal response to tests. The correlation of all the chemical evidence yielded by the application of one or two reagents



may advance the analysis far beyond the direct "positive or negative" results of the tests.

To this end it is desirable that full notes of the results of all tests with group or specific reagents should be kept, especially since even negative evidence, or abnormal and unexpected precipitates, may acquire a significance and afford valuable confirmation in the light of subsequent operations. Furthermore, the evidence thus assembled in concrete form is particularly useful as an aid in deciding what crucial tests should be applied to decide doubtful cases. The analyst should never perform a test without having in his mind a clearly formulated question which he expects it to answer.

It is not possible to generalize as to whether one should test first for cations or anions. Whichever reactions seem most likely to yield conclusive information should be tried first. Sometimes it is quickest to carry out both types of tests more or less together; frequently the recognition or elimination of certain cations will immediately indicate the presence or absence of certain anions, and *vice versa*. A great saving of time will result if each step in the analysis can be utilized as a guide to the choice of the next, and can be correlated with those which have preceded it.

It is always wise to reserve the major portion of the sample, and to carry out the analysis on a fraction of it. If the analyst has schooled himself in carrying out tests on minute drops of solutions, this will entail no hardship, and will ensure that ample material is available for confirmatory reactions, or in case unexpectedly extensive tests need to be carried out. Similar precaution is advisable when dealing with filtrates or precipitates which are to be used for subsequent tests.

The slides, crucibles, and watch-glasses which serve as the apparatus of the analysis may conveniently be marked by a "glass marking" or tungsten-carbide pencil, in order to avoid confusing preparations which are set aside for future study.

As a preliminary to the actual analysis, the common chemical properties of the material should be noted, such as solubility in various solvents and reaction with them, behavior on heating the dry substance and its solution, ease of sublimation or fusibility, acid or alkaline character of the aqueous solution, etc. Tables of properties<sup>7</sup> will be found invaluable for reference in connection with such examinations, and especially for confirming or disproving tentative identifications based on analytical reactions.

<sup>7</sup> Such as Segerblom: *Tables of Properties of Inorganic Substances*, and the larger works on inorganic chemistry and qualitative analysis.

Reagents for microscopical analysis are ordinarily applied to material in solution, but fusion reactions and blowpipe tests may often be employed to great advantage, especially in dealing with minerals or relatively insoluble substances.

Where a **positive test** is obtained, the interpretation is usually simple, provided the analyst actually is familiar, from experience on knowns, with the character of the product. However, when a search is made for any particular element or radical, care should be taken that none has been introduced in the solvents, reagents, or apparatus used, or a positive test will be of doubtful meaning. For this reason blank tests run in parallel are always advisable in critical work.

Rough estimations of the amount of the substance present are often possible from the heaviness of the precipitate which it yields, and also from the limits of sensitivity of the various tests for the ion in question.

Where a definite precipitate not recognizable as due to any of the substances sought occurs, several explanations are possible.

1. The reagent may be yielding a precipitate with the ion of opposite sign. For example, potassium mercuric thiocyanate as a test for cations in a solution containing an iodide would give a precipitate of mercuric iodide, which might be misinterpreted as indicating the presence of an ion forming an insoluble double thiocyanate.

2. Too concentrated solutions, resulting in too rapid precipitation, may have prevented the growth of crystals of a size adequate for recognition. The method of adding the reagent is an important factor in regulating the concentration gradient in the preparation. All parts of the test drop should be examined, since in some at least there are likely to be crystals of characteristic form.

3. The presence of a strong acid or alkali may prevent precipitation. This is particularly likely to occur if acid has been used to dissolve the material. For example, an insoluble phosphate, dissolved in  $\text{HNO}_3$ , will yield no precipitate with  $\text{AgNO}_3$  unless the free acid is neutralized. Buffer salts, such as  $\text{NH}_4\cdot\text{C}_2\text{H}_3\text{O}_2$ , are often useful in lowering the hydrogen-ion concentration of the solution sufficiently to allow precipitation to occur.

4. Other substances in test drops may interfere with the normal habit or color of the reaction product. Combinations of ions sometimes act in a manner not to be predicted from their individual behavior.

5. The precipitate upon which the test depends may be masked by the simultaneous precipitation of other materials. For instance, hydrous oxides may be precipitated in making the solution alkaline preparatory to a test.

6. Ions not ordinarily precipitable by the reagent may be present in

excessive amount, and hence form relatively insoluble compounds or double salts of low solubility; or some substance may be "salted out." This is particularly likely to occur if too concentrated solutions are used, or if the test drop is allowed to evaporate to dryness.

7. Some substance not previously known to react under the conditions of the test may be present.

**Negative tests** are not always to be interpreted as signifying the absence of the substance sought.<sup>8</sup> Lack of positive results may be due to any of a number of reasons, the most common of which are as follows:

1. The substance sought may be absent, or present, in quantity below the limit of the reaction employed.

2. Its *effective* concentration may be too low, owing to its presence in a complex ion or insoluble or undissociated compound.

3. Precipitation may be inhibited by high acidity or alkalinity, solubility in excess of reagent, or the presence of other interfering substances.

4. The substance may have been decomposed or lost in the process of solution or evaporation, or in other preliminary stages of the analysis.

5. The reagent may not have been applied in the proper manner.

6. The conditions existing in the test drop may have been such as completely to alter the habit of the crystals whose separation constitute the test.

**Substances insoluble in water** are likely to be fairly easy to identify after they have been "opened up" or brought into solution, for the very fact of their insolubility limits the possibilities, once some chemical information is available.

Frequently such materials are natural or synthetic minerals, and a knowledge of the methods of identification by "bead" tests, blowpipe reactions, and other methods of the mineralogist affords a great saving of time and labor. The probable associations of elements in minerals will also be a guide to further testing.

The following procedures will be found adequate for dealing with most insoluble materials,<sup>9</sup> but it must be borne in mind that the anion of the substance tested may be affected by them.<sup>10</sup>

1. Treatment with  $\text{HNO}_3$ . Use dilute acid and warm gently, replac-

<sup>8</sup> See Staples: *Amer. Mineralogist* 21, 615 (1936).

<sup>9</sup> See also Feigl: *Mikrochemie* 20, 198 (1936).

<sup>10</sup> Repeated evaporations with concentrated acids, or long heating with volatile solvents, may result in a concentration of the small amounts of impurities present in these liquids, to a point where they yield positive tests. Blank treatments will eliminate the risk of misinterpretations due to such causes.

ing evaporation losses. If undissolved, employ concentrated  $\text{HNO}_3$  and heat to boiling. The material may be converted to nitrates or oxides.

Evaporate some of the  $\text{HNO}_3$  solution to dryness, to note the amount dissolved, and the possible presence of isotropic crystals (Ca, Sr, Ba, Pb nitrates, or  $\text{As}_2\text{O}_3$ ).

2. Treatment with aqua regia may be successful if  $\text{HNO}_3$  fails as a solvent. The material may be converted to chlorides.

3. Concentrated  $\text{H}_2\text{SO}_4$  may serve to dissolve insoluble sulphates, and their cations may be recognized on recrystallization from it. (See page 110.) Salts of volatile acids will be converted to sulphates.

4. Alkalis such as  $\text{NaOH}$  or  $\text{KOH}$ , in solution, or used for fusions in a tiny cup of silver, nickel, or iron, sometimes serve for "opening up" minerals. Anions are likely to be transposed more or less completely by such treatment.

$\text{Na}_2\text{CO}_3$  in concentrated solution may, on long boiling, effect a transposition of ions. All or part of the anions will be present as soluble sodium salts, and the cations as insoluble oxides or carbonates.  $\text{Na}_2\text{CO}_3$  is also useful for fusions.

5.  $\text{HF}$ ,  $\text{NH}_4\text{F}\cdot\text{HF}$ , or  $\text{NaF}$  and  $\text{H}_2\text{SO}_4$ , are useful in dealing with insoluble oxides or silicates. Reactions with fluorides should be employed only as a last resort, on account of the risk of injury to lenses.

6. Heating with  $\text{HI}$  of sp. gr. 1.7 will bring into solution many compounds not easily "opened up" by other treatments.<sup>11</sup>

Substances soluble in water, or solutions obtained from the treatment of insoluble materials, may be tested according to various procedures, depending on the completeness of the information desired.

Tests for the presence or absence of a single ion require only that the solution shall be of the optimum concentration to yield a conclusive test, and that interfering substances shall be absent. In dealing with material of unknown composition, various concentrations of sample and of the reagent should be tried. Care should be taken to avoid the presence of strong acids, if the precipitate sought is the salt of a weak acid.

More than one reagent should be used in most cases, especially if the results are at all doubtful, and it is well to transform the precipitate first obtained successively into several different characteristic compounds of the material found, as confirmation of its identity.

It may happen, as in spectroscopic analysis, that traces of impurities are only detectable after a preliminary chemical separation from the substance which constitute the bulk of the sample. Frequently microscopical tests can be employed in connection with operations on a larger

<sup>11</sup> Caley and Burford: *Ind. Eng. Chem. Anal. Ed.* 8, 63 (1936).

scale, as in the identification of small amounts of precipitates obtained in macroscopical qualitative analysis. The procedures of inorganic and analytical chemistry appropriate to such separations or concentrations will depend on the nature of the sample and of the ions to be tested for, and cannot be discussed here.

**Tests for members of a group** are often valuable as rapid means of furthering the course of the analysis, or of eliminating a number of possibilities at once. Reagents such as metallic zinc or magnesium, "zinc sulphide fibers," ammonium hydroxide, hexamethylenetetramine, or potassium xanthate may serve to point the way to subsequent identity tests for individual cations. More specific reagents, such as cesium chloride, potassium mercuric thiocyanate, oxalic acid, hydrochloric acid, or sulphuric acid, may be used similarly, and will frequently serve for specific identifications, confirmatory tests being applied if necessary. Such group tests will ordinarily be applied on separate small portions of the solution, though in some instances it may be feasible to add a second reagent to a drop in which no positive results have been obtained in the first test.

In identifying anions the reagents of the Bunsen-Treadwell system,  $\text{BaCl}_2$  and  $\text{AgNO}_3$ , are employed in like manner. It may sometimes be useful to test for the anions of volatile acids, by heating with  $\text{H}_2\text{SO}_4$  or  $\text{HC}_2\text{H}_3\text{O}_2$ .

**Tests for cations**, as employed in microscopical qualitative analysis, will not ordinarily be carried out in a fixed sequence or in accordance with a systematic analytical scheme. Instead, the preliminary tests with the group reagents mentioned above will point fairly positively to a limited number of possibilities, and these should then be sought by means of identity tests. In general, it is well to make a list of all the ions which may be present and to check off from this list all those individuals or groups which have been positively eliminated. Otherwise there is a likelihood that the analyst may neglect to test for certain ions which do not appear in the various groups.

A single solid phase should not be assumed to be a simple salt; it may be a double or mixed salt, or a solid solution. The probable associations of ions in such cases will afford a useful guide to judicious testing; for instance, most double salts contain one of the alkali metals, and solid solutions ordinarily contain ions belonging to the same chemical family or at least having like valence.

**Examination of Alloys.**<sup>12</sup> — The material, in the form of fine filings or borings, is dissolved in a tiny crucible or watch-glass, by means of

<sup>12</sup> For the identification of metal fragments, see Lockwood: *Analyst* 59, 812 (1934).

the appropriate solvent. A streak on a plate of ground glass may be dissolved by adding a drop of solvent, and decanting. A very minute amount of metal will yield several drops of a relatively concentrated solution.

Non-ferrous alloys are best dissolved in  $\text{HNO}_3$ . Sn (and possibly Sb, P, As, W, Si, Ti, and Zr) may remain as an insoluble oxide residue, which may adsorb some of the soluble nitrates. It is essential that all the metal shall have been brought into solution, lest some of the more noble constituents "plate out" upon the undissolved portion.

Separations and tests may be carried out according to the following schemes, but every possible short cut should be utilized.

### Scheme for the Qualitative Analysis of Common Non-Ferrous Alloys<sup>13</sup>

Dissolve in concentrated  $\text{HNO}_3$ . Evaporate to a syrupy consistency or to a moist mass on water bath. Do not carry to complete dryness. Add water and again evaporate. Extract with *warm* water. Filter.

*Residue A* As; Sb; Bi; Sn

(Traces of Pb; Cu etc.) Remove a little of the residue and test it for As by conversion into  $\text{H}_3\text{As}$ . (See page 222.)

Dissolve the remainder of residue *A* in aqua regia. Divide into three parts.

1. Test with  $\text{CsCl}$ . Or reduce with metallic Fe to  $\text{SnCl}_2$  and test for Sn.

2. If Sn is absent, test for Sb with  $\text{CsCl}$ ; if Sn is present, test for Sb by Method B, page 232.

3. Test with  $\text{CsCl}$  and confirm by conversion into sodium or potassium bismuth sulphate.

*Filtrate I* Add  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  Filter = *Filtrate III*. Precipitate *B*.

*Precipitate B* Fe; Cr; Al; Pb; Hg

Dissolve in the least possible volume of dilute HCl. Add NaOH in excess. Add  $\text{Na}_2\text{O}_2$ , boil, filter = *Filtrate II*. Precipitate *C*.

*Precipitate C* Hg, Fe

Dissolve in dilute HCl. Divide into two parts.

1. Test for Hg with KI. Or treat with metallic copper, sublime the Hg, and convert the globules into  $\text{HgI}_2$  with iodine. (See page 154.)

2. Test for Fe with  $\text{KSCN}$  or  $\text{K}_4\text{Fe}(\text{CN})_6$ .

<sup>13</sup> Method of Whitmore and Schneider: *Ind. Eng. Chem. (Anal. Ed.)* 2, 173 (1930). Slightly modified.

*Filtrate II* Al; Pb; Cr

Acidify with acetic acid. Divide into three parts.

1. Test for Pb with KI after adding  $\text{HNO}_3$ .

2. Test for  $\text{CrO}_4^{--}$  with  $\text{AgNO}_3$  (see page 368). (Silver acetate may be precipitated.)

3. Precipitate all the lead as  $\text{PbSO}_4$ . Centrifuge. Concentrate. Test for Al with  $\text{Cs}_2\text{SO}_4$ . (See page 176.)

*Filtrate III* Mn; Ni; Co; Zn

Add  $\text{H}_2\text{O}_2$ , boil and filter = *Filtrate IV*. Precipitate *D*.

*Precipitate D* Mn; Co; Ni

Divide into three parts.

1. Fuse with  $\text{Na}_2\text{CO}_3$ ; green color = Mn. Or test for Mn with sodium bismuthate. (See page 260.)

2. Dissolve in HCl and test for Ni with dimethylglyoxime. (See page 274.)

3. Dissolve in HCl and test for Co with  $\text{K}_2\text{Hg}(\text{SCN})_4$ . (See page 269.) Or test with sodium nitrite. (See page 270.)

*Filtrate IV* Cu; Zn; Cd; Ni; Mg

Acidify with HCl. Add  $\text{Na}_2\text{SO}_3$  and  $\text{NH}_4\text{SCN}$ , boil and filter = *Filtrate V*. Precipitate *E*.

*Precipitate E* Cu

Dissolve in HCl. Test for Cu with  $\text{K}_2\text{Hg}(\text{SCN})_4$ . (See page 136.)

*Filtrate V* Zn; Cd; Ni; Mg

Add  $\text{NH}_4\text{OH}$  in slight excess. Divide into three parts.

1. Acidify with HCl. Test for Zn, Cd, with  $\text{K}_2\text{Hg}(\text{SCN})_4$ . (See page 136.)

2. Test for Ni with dimethylglyoxime.

3. Add  $\text{HNa}_2\text{PO}_4$ . Decant, filter, or centrifuge. Dissolve the precipitate in the least amount of HCl. Reprecipitate the Mg as  $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$  with  $\text{NH}_4\text{OH}$ . Or add  $\text{NaC}_2\text{H}_3\text{O}_2$  and  $\text{HC}_2\text{H}_3\text{O}_2$  and test with  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ . (See page 130.)

Noble metals, and members of the platinum group, may be analyzed by the methods suggested on pages 301 and 303.<sup>14</sup>

Ferrous alloys are best attacked by HCl or  $\text{H}_2\text{SO}_4$  (dilute). Stainless steels and other acid-resistant alloys may require treatment with aqua regia. The analysis can conveniently be based upon the following scheme.

<sup>14</sup> See also the methods of Strebinger and Holzer: *Mikrochemie* 8, 264-70 (1930).

Scheme for the Qualitative Analysis of Ferrous Alloys<sup>15</sup>

Dissolve the filings or borings in a very small volume of  $\text{H}_2\text{SO}_4$  (1 : 3) in a *covered* crucible (Fig. 10). Warm gently until completely dissolved; then add a little more of the sample, cover tightly, and allow to stand until *all* the iron is reduced to the ferrous condition. Dilute and filter; wash the residue with acidulated water. Work quickly to prevent oxidation.

*Residue A* W; Si; C

Together with traces of other elements. Fuse with  $\text{K}_2\text{S}_2\text{O}_7$ . Extract the fusion with water acidulated with  $\text{H}_2\text{SO}_4$ . Filter; discard filtrate.

*Residue B* W; Si

Test (see page 190). Remove Si as  $\text{SiF}_4$ . Ignite residue =  $\text{WO}_3$ . Test by Methods B, C, pages 192, 194.

*Filtrate I*, from *Residue A*

Fe; Al; Ti; Zr; Mo; U; V; As; P; Cr

Add  $\text{NH}_4\text{OH}$ , *carefully avoiding an excess*. Filter. If all the Fe is in the ferrous condition and no excess of  $\text{NH}_4\text{OH}$  is added, the filtrate will consist of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$  in solution. *Residue C*.

*Residue C*

Dissolve in the least amount possible of  $\text{HNO}_3$  (1 : 1). Add  $\text{Na}_2\text{O}_2$  until all the  $\text{HNO}_3$  is neutralized. Add  $\text{Na}_2\text{CO}_3$ ; warm gently; *Filtrate II*. *Precipitate D*.

*Precipitate D* Fe; Ti; Zr (with a small amount of V and P.)

Wash with a solution of  $\text{NH}_4\text{NO}_3$ . Dissolve in  $\text{H}_2\text{SO}_4$  (1 : 5). Test for Ti and Zr. (See pages 194, 198.)

*Filtrate II* Al; Mo; U; V; As; P; Cr (with traces of Ti and Zr)

Evaporate to small volume. Add  $\text{HNO}_3$  (1 : 1) until almost neutral. This should precipitate Al as hydrous oxide or phosphate or both, providing that the Al is in considerable excess of the P (about 10 : 1). Add to the turbid solution  $(\text{NH}_4)_2\text{CO}_3$ . Allow to stand a short time. Filter = *Filtrate III*. *Precipitate E*.

*Precipitate E* Al; P

Wash. Test one portion for Al by cesium sulphate. Test another portion for P. (See page 220.)

<sup>15</sup> Based upon methods of Moore and co-workers: Bul. 212, *Bureau of Mines*, Washington, 1923.



*Filtrate III* Mo; U; V; As; P; Cr (Ti, Zr)

Acidify with  $\text{HNO}_3$ . Boil to remove  $\text{CO}_2$ . Add  $\text{NH}_4\text{OH}$  (1 : 1). Acidify with  $\text{HNO}_3$ . Add  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  and  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ . Filter = *Filtrate IV*. Precipitate *F*.

*Precipitate F* Mo; V; As; Cr

Dissolve in  $\text{HNO}_3$ . Fume with  $\text{H}_2\text{SO}_4$ ; dilute; filter or centrifuge to remove  $\text{PbSO}_4$ . Test for As by conversion into  $\text{H}_3\text{As}$ , page 222. For Cr by conversion into  $\text{CrO}_4^{--}$ .

For V by conversion into ammonium metavanadate and recrystallization from acetic acid.

*Filtrate IV* U

Remove the Pb as  $\text{PbSO}_4$ . Precipitate the U with  $\text{NH}_4\text{OH}$ , giving ammonium uranate.

Tests for anions should be carried out according to the Bunsen-Treadwell system. (See page 316.) The original solution of the unknown may be used, or that obtained on transposition with  $\text{Na}_2\text{CO}_3$ , in which only the sodium salts of the various acids are present. It is necessary to bear in mind that treatment with strong acids or oxidizing agents, fusions, interaction with other anions, or even exposure to the air may cause alteration of an anion and invalidate the ultimate tests.

In general it is advisable first to separate the great groups, with  $\text{AgNO}_3$  and with  $\text{BaCl}_2$ , and to treat the resulting precipitate further with  $\text{HNO}_3$  or other acid, and with whatever specific reagents can be properly applied, in order to identify the anions present.



## APPENDIX

### PREPARATION OF SPECIAL REAGENTS

**Preparation of Potassium Mercuric Thiocyanate.**—The potassium double salt  $K_2Hg(SCN)_4$  is preferable to the corresponding ammonium and sodium salts, which are deliquescent. It is of higher solubility than  $KHg(SCN)_3$ , and occurs as monoclinic tablets.<sup>1</sup> Either of the following methods of preparation is satisfactory:

1. Dissolve a known amount of KSCN in a small volume of water; add the equivalent quantity of freshly precipitated and washed  $Hg(SCN)_2$ . (Do not use the material which is marketed in stick form.) Dilute, with stirring, until complete solution is obtained, and evaporate to dryness at room temperature, preferably in a desiccator.

2. Dissolve 3 to 5 parts of KSCN and 1 part of  $Hg(SCN)_2$  in a minimum quantity of water, and evaporate in a desiccator. Collect the first crop of tabular crystals, wash with alcohol, and dry.

**Preparation of Potassium Ethyldithiocarbonate (Potassium Xanthate).<sup>2</sup>**—To 25 cc. of 95 per cent alcohol add 5 grams of KOH. Warm gently until no more KOH dissolves. Cool and decant the clear, supernatant solution. Add 10 cc. of carbon disulphide. Shake thoroughly in a stoppered flask. Chill in ice water until the potassium ethyldithiocarbonate has completely separated, and while the preparation is still cold add sufficient ether to dissolve the unacted-upon alcohol and carbon disulphide. Filter upon a Witt plate or Buchner funnel. Suck dry and wash the fine crystals thoroughly with ether. Spread out the crystal upon filter paper until the ether has evaporated and transfer to a well-stoppered container.

**Preparation of Cesium Sulphate.**—To a small volume of dilute sulphuric acid add cesium chloride in an amount very slightly in excess of that required to convert all the  $SO_4$  to  $Cs_2SO_4$ . Heat gently and when dry slowly raise the temperature until fumes of  $SO_3$  just begin to appear. Cool, dissolve in water, and evaporate to crystallization.

**Preparation of Fibers Impregnated with Litmus.**—A good quality of raw silk is boiled in water containing a little soap, rinsed thoroughly, and placed for two hours at room temperature in a sodium hydroxide solution containing 10 grams sodium hydroxide in 100 cc. of water. The silk is then thoroughly washed with

<sup>1</sup> The physical chemistry of the double thiocyanates of potassium and mercury is discussed by Mason and Forgeng: *Jour. Phys. Chem.* 35, 1123 (1931).

<sup>2</sup> Kotten: *Chemist-Analyst*, No. 48, Nov.-Dec., 1926.

distilled water. Dyeing this treated silk in a 10 per cent solution of purified litmus,<sup>3</sup> acidified with 3 or 4 drops of 1 : 4 sulphuric acid, produces a fiber of the proper color intensity. In order to dye the silk properly, the acid litmus solution containing it is evaporated to a thick syrup, the silk then removed and washed in running water, neutralized carefully with very dilute sodium hydroxide solution, and again washed thoroughly. If red and blue varieties of the silk are desired, these neutral-tinted fibers may be treated with dilute acetic acid for red or with dilute sodium hydroxide for blue, and then washed thoroughly in running water.

The sensitiveness of the litmus silk depends upon the degree of adsorption of the dye, the degree of purification of the raw silk, and the degree of purification of the litmus.

If too little dye is adsorbed, the color change is not distinct enough. If too much dye is adsorbed, the fiber becomes less sensitive, and the color is so deep that it renders the fiber opaque.

The greater the degree of purification of the litmus, the more sensitive the dyed fiber, though this factor is not as important as the two former ones.

**Preparation of Purified Litmus.**—The following procedure (essentially Wartha's method)<sup>4</sup> is suggested for obtaining an exceedingly pure litmus. Commercial litmus "cubes" are extracted with 95 per cent alcohol until the alcoholic extract no longer has a reddish tinge. They are then repeatedly extracted with water until the greater part of the coloring matter is removed, a current of air being blown through the solution to prevent reduction. The filtered solution is carried to a thick syrup in an evaporator on the water bath. The mass is then evaporated several times with portions of absolute alcohol acidified with acetic acid in order to destroy carbonates, and the residue is extracted repeatedly with absolute alcohol as long as the alcohol has a reddish color by reflected light. The residue is dissolved in water, concentrated to a thick syrup, and treated with absolute alcohol. The pasty mass is stirred with absolute alcohol until the portions poured off no longer contain any red coloring matter. The final residue is dissolved in distilled water, concentrated to a thick syrup, and poured into absolute alcohol. The semi-solid gummy precipitate is spread on a plate and dried at 70° to 80° C. The pigment as thus obtained forms a hard tenacious mass, easily soluble in water, and yields an indicator of great sensitiveness, changing at once to red or blue with acid or alkali.

**Preparation of Fibers Impregnated with Congo Red.**—Of the common textile fibers tested, silk and viscose were found to be the most suitable for the preparation of Congo red fibers, the latter giving an even more sensitive fiber than the former.

The best concentration of the dye for the silk fibers was found to be a 0.5 per cent solution, made alkaline with sodium hydroxide. For the preparation of the Congo red viscose-silk fibers, a somewhat more concentrated solution is advisable. Dyeing in a 2 per cent alkaline solution of Congo red for 15 minutes, washing thoroughly, and then drying by pressing between filter papers was found to yield an eminently satisfactory fiber.

Congo red fibers can be used in the red form only, as the blue form is unstable in the air. For the detection of acidity they compare favorably with the litmus fibers, having the same degree of sensitiveness.

<sup>3</sup> Chamot and Cole: *Jour. Ind. Eng. Chem.* 9, 969 (1917).

<sup>4</sup> *Berichte* 9, 217 (1876).

Although Congo red is employed as an indicator in analytical work for the purpose of differentiating between organic and inorganic acids, Congo red fibers are far too sensitive for this purpose.

**Preparation of Fibers Impregnated with Turmeric.**—Of the various fibers tested, viscose silk gives by far the best color reaction, flax being next best but less satisfactory in comparison. No preliminary treatment of the viscose silk to render it more adsorptive is necessary.

A 50 per cent alcoholic, alkaline solution of turmeric is prepared by boiling approximately 20 g. of ground turmeric root with 50 cc. of alcohol and adding to the filtered solution an equal volume of water and  $\frac{1}{2}$  to 1 cc. of dilute sodium hydroxide (10 per cent). The fibers are immersed in this solution, which is then evaporated on a water bath<sup>5</sup> to a syrupy consistency. The fibers are removed and immediately dipped in 95 per cent alcohol, pressed between filter paper, dipped in a dilute aqueous solution of sulphuric acid, washed with water, and dried. The transference of the fibers from the hot dye to the alcohol must be done quickly as otherwise the turmeric adhering to the fibers is removed only with difficulty. Too long an immersion in the alcohol tends to remove the adsorbed dye as well as the excess dye.

If the fiber still appears to have any unadsorbed turmeric adhering to it (with viscose silk this is easily noted by the lack of luster), it can once more be dipped in alcohol and washed with water. Any unadsorbed turmeric interferes with the formation of the blue color in the boron test. This method as given yields a beautiful golden-yellow product which was found to be eminently satisfactory.

**Preparation of Wool Impregnated with Zinc Sulphide.**—The defatted wool is swelled by soaking over night at room temperature, in a 1 per cent solution of sodium hydroxide. It is then washed and dipped 5 or 6 times alternately in solutions of 10 per cent zinc acetate and 10 per cent sodium sulphide, pressing out the excess solution but not washing between dippings. After the final dipping, the impregnated wool is washed and dried by pressing between filter paper. Zinc sulphide wool fibers made in this way are sensitive to 1  $\mu$ g. of copper per drop. The sodium sulphide solution should be freshly prepared by passing  $H_2S$  into a solution of  $NaOH$ , until a portion removed fails to yield a precipitate with  $MgCl_2$ . The fat may be removed from the wool by a mixture of alcohol and ether.

**Preparation of Benzyl-pseudo-thiourea**— $C_6H_5CH_2 \cdot NH \cdot CS \cdot NH_2$ .<sup>6</sup>—Dissolve 76 grams (1 mole) of thiourea in 200 cc. of 40 per cent alcohol. Add with constant stirring 126.5 grams (1 mole) of benzyl chloride. Warm gently to start the reaction. Warm for a short time, then cool. Benzyl-pseudo-thiourea crystallizes out. Filter with suction and recrystallize from 40 per cent alcohol. The compound exists in two modifications, a stable form melting at  $144^\circ$  which solidifies to a metastable form melting at  $175^\circ$ .

This reagent is employed in microscopical qualitative analysis in the form of its hydrochloride in solution.

<sup>5</sup> When preparing or working with fibers impregnated with turmeric, all contact with "resistance" (Pyrex type) glass vessels or object slides is to be avoided, since glass of this variety usually contains boron.

<sup>6</sup> Bernthsen and Klinger: *Ber.* 12, 574 (1879).

Chambers and Scherer: *Ind. Eng. Chem.* 16, 192 (1924).

Hann and Keenan: *Jour. Phys. Chem.* 31, 1082 (1927).

Dissolve 5 grams of benzyl-pseudo-thiourea in 50 cc. of distilled water containing 1 cc. of concentrated HCl.

The hydrochloride crystallizes upon an object slide in thin rhombs and tablets whose acute angles are  $74^\circ$ . When free HCl is present, curious plates and prisms are obtained with very characteristic twins so oriented as to exhibit a re-entrant angle.

**Preparation of Nickelous Ethylenediamine Nitrate** —  $[\text{Ni}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_3] \cdot (\text{NO}_3)_2$ .<sup>7</sup> — Dissolve 1 gram of  $\text{Ni}(\text{NO}_3)_2$  in 5 cc. of distilled water. Add ethylenediamine until the solution acquires a purple color.

This reagent reacts with thiosulphates and dithionates but with no other anions of the Sulphur Group.

<sup>7</sup> Spacu and Spacu: *Zeit. anal. Chem.* **89**, 192 (1932).

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(For works of a more general character the reader is referred to *Volume I* of this Handbook, pages 449-451.)



PERIODIC TABLE OF THE CHEMICAL ELEMENTS—1929  
THE FIGURE ABOVE THE NAME OF EACH ELEMENT IS ITS ATOMIC NUMBER AND THAT BELOW, ITS ATOMIC WEIGHT

Period	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
I		1 Hydrogen H 1.008							
II	2 Helium He 4.0	3 Lithium Li 6.94	4 Beryllium Be 9.02						
III	10 Neon Ne 20.2	11 Sodium Na 23.00	12 Magnesium Mg 24.32	13 Aluminum Al 26.9	14 Silicon Si 28.06	15 Phosphorus P 31.04	16 Sulphur S 32.06	17 Chlorine Cl 35.46	
IV	18 Argon Ar 39.94	19 Potassium K 39.10	20 Calcium Ca 40.07	21 Scandium Sc 45.10	22 Titanium Ti 47.90	23 Vanadium V 50.98	24 Chromium Cr 52.01	25 Manganese Mn 54.93	26 Iron Fe 55.84
		29 Copper Cu 63.57	30 Zinc Zn 65.38	31 Gallium Ga 69.72	32 Germanium Ge 72.60	33 Arsenic As 74.90	34 Selenium Se 79.20	35 Bromine Br 79.92	27 Cobalt Co 58.94
		37 Rubidium Rb 85.44	38 Strontium Sr 87.63	39 Yttrium Yt 88.92	40 Zirconium Zr 91.22	41 Columbium Cb 93.10	42 Molybdenum Mo 98.00	43 Manganese Mn 54.93	45 Rhodium Rh 102.91
V	36 Krypton Kr 82.90	47 Silver Ag 107.8	48 Cadmium Cd 112.41	49 Indium In 114.80	50 Tin Sn 118.70	51 Antimony Sb 121.77	52 Tellurium Te 127.50	53 Iodine I 126.92	46 Palladium Pd 106.70
		55 Cesium Cs 132.81	56 Barium Ba 137.37	57-71 Rare Earths*	72 Hafnium Hf 178.60	73 Tantalum Ta 181.60	74 Tungsten W 184.00	75 Rhenium Re 188.7	77 Iridium Ir 193.10
VI	54 Xenon Xe 130.20	79 Gold Au 197.20	80 Mercury Hg 200.61	81 Thallium Tl 204.39	82 Lead Pb 207.22	83 Bismuth Bi 209.00	84 Polonium Po (210)	85 Astatine At (210)	78 Platinum Pt 196.23
		87 Francium Fr (223)	88 Radium Ra 226.95	89 Actinium Ac (227)	90 Thorium Th 232.15	91 Uranium U 238.03	92 Uranium X (Brevium)		
VII	86 Radon Rn 222.00								

\* Rare Earths

57 Lanthanum La 138.90	58 Cerium Ce 140.25	59 Praseodymium Pr 140.92	60 Neodymium Nd 144.27	61 Promethium Pm (145)	62 Samarium Sm 150.43	63 Europium Eu 152.00	64 Gadolinium Gd 157.25
65 Terbium Tb 158.92	66 Dysprosium Dy 162.50	67 Holmium Ho 164.93	68 Erbium Er 167.26	69 Thulium Tm 168.93	70 Ytterbium Yb 173.05	71 Lutetium Lu 175.00	

## LABORATORY CHEMICAL MICROSCOPY — CORNELL UNIVERSITY

## KEY TO REAGENTS IN REAGENTS BLOCKS

	1	2	3	4	5	6	7	8	9	10	11	12	
A	Silver Nitrate	Thallous Nitrate	Potassium Thiocyanate	Calcium Acetate	Potassium Sulphate	Sodium Sulphate	Sodium Bicarbonate	Potassium Chlorate	Potassium Bichromate	Oxalic Acid	Litmus Silk	Ammonium Fluoride	A
B	Chloroplatinic Acid	Perchloric Acid	Dimethyl Glyoxime	Cobalt Acetate	Mercurous Nitrate	Mercuric Chloride	Ammonium Carbonate	Ammonium Persulphate	Potassium Chromate	Potassium Oxalate (Acid)	Antimony Chloride	Cesium Sulphate	B
C	Barium Chloride	Hydroxylamine HCl	Strontium Acetate	Copper Acetate	Potassium Nitrate	Lead Acetate	Sodium Carbonate	Ammonium Chloride	Potassium Ferrocyanide	Ferrie Chloride	Hexamethylene tetramine	Nitron Sulphate	C
D	Cesium Chloride	Phenylene-diamine HCl	Sodium Bismuthate	Zinc Acetate	Sodium Thio-sulphate	Arsenic Acid	Potassium Xanthate	Citric Acid	Potassium Permanganate	Magnesium Chloride	Turnerite Viscose-silk	Copper	D
E	Potassium Mercuric cyanate	Potassium Iodide	Sodium Hydroxide	Sodium Acetate	Ammonium Acetate	Uranyl Acetate	Bismuth Sulphate	Di-sodium Phosphate	Ammonium Molybdate	Starch	Zinc Sulphide Wool	Zinc	E
	1	2	3	4	5	6	7	8	9	10	11	12	
Arsenic Acid.....6D													
Ammonium Carbonate.....5E													
Barium Chloride.....7B													
Calcium Chloride.....8C													
Cesium Chloride.....9E													
Cobalt Chloride.....12A													
Copper Chloride.....9B													
Copper Sulphate.....10C													
Cesium Chloride.....11B													
Cesium Sulphate.....7E													
Cesium Acetate.....4A													
Cesium Chloride.....11D													
Cesium Sulphate.....12B													
Chloroplatinic Acid.....1B													
Citric Acid.....8D													
Cobalt Acetate.....4B													
Copper Metal.....12D													
Copper Acetate.....4C													
Dimethyl Glyoxime.....3B													
Ferrie Chloride.....11C													
Hexamethylene-tetramine.....10C													
Hydroxylamine HCl.....11C													
Lead Acetate.....2C													
Litmus Silk.....11A													
Magnesium Chloride.....10D													
Mercuric Chloride.....6B													
Mercurous Nitrate.....12C													
Nitron Sulphate.....10A													
Oxalic Acid.....10A													
Perchloric Acid.....2B													
Cobalt Acetate.....4B													
Copper Metal.....12D													
Copper Acetate.....4C													
Dimethyl Glyoxime.....3B													
Ferrie Chloride.....11C													
Hexamethylene-tetramine.....10C													
Hydroxylamine HCl.....11C													
Lead Acetate.....2C													
Litmus Silk.....11A													
Magnesium Chloride.....10D													
Mercuric Chloride.....6B													
Mercurous Nitrate.....12C													
Nitron Sulphate.....10A													
Oxalic Acid.....10A													
Perchloric Acid.....2B													
m-Phenylenediamine HCl.....2D													
Potassium Bichromate.....9A													
Chlorate.....8A													
Chromate.....9C													
Ferrocyanide.....9C													
Iodide.....11E													
Mer. Thiocyanate.....11E													
Nitrite.....5C													
Oxalate.....10B													
Permanganate.....9D													
Starch.....10E													
Strontium Nitrate.....3C													
Thallous Nitrate.....2A													
Turnerite Viscose-silk.....11D													
Uranyl Acetate.....4E													
Zinc Acetate.....12E													
Metal.....12E													
Sulphide Wool.....11E													
Silver Nitrate.....7D													
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CAUTION. — Never remove from the block more than one vial at a time. Use special care to avoid mixing stoppers and contaminating reagents.

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